Assessing the impact of urbanization on White River water and sediment geochemistry in an agricultural watershed

Dean C. Snidow
Department of Geological Sciences
Ball State University

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Acknowledgements

This project was made possible by funding from the Geologic Society of America, a research grant from the Office of Academic Research and Sponsored Programs at Ball State University and the Department of Geological Sciences at Ball State University.

I would like to thank Dr. Klaus Neumann, my thesis advisory, for his help and guidance throughout the course of this study. Without his ideas and suggestions, I would have been lost. I also need to thank the rest of my committee, Dr. Jeffry Grigsby and Dr. Alan Samuelson, who provided suggestions and assisted with editing the thesis.

Special thanks to Dr. Carolyn Dowling, Department of Chemistry and Physics, Arkansas State University and Dr. Melody Bernot, Department of Biology, Ball State University for use of lab space and equipment, as well as extra encouragement and help.

I need to thank my parents, Chris and Sondra, and my sister, Kathryn. Thank you for the love and support that you have given me throughout my time at Ball State. Without the constant encouragement, I might not have finished this project. I also want to thank Grandpa for his check-up calls.

I also need to thank Ms. Kelli McGuire, who accompanied me on a couple of the sampling trips. She helped with collecting samples and taking pictures among other things. She also provided support and, when needed, tough love throughout.

I also want to thank the McGuire and Hartley families for their friendship and hospitality, and for being my family away from home. And finally, I have to thank John Lozar. His company and friendship while trying to hunt down Virginia Tech games on television was irreplaceable, and I thank him for the enthusiasm.

I. Introduction

Increased urbanization in the United States and the rest of the world has led to increased research on its impact on the local ecology and watersheds (Walsh et al. 2005). Urbanization here is defined as the clearing of natural vegetative cover followed by the construction of an impervious cover (Ryan and Packman 2005). In the U.S. between 1992 and 1997, 6.5 million hectares (about 16 million acres) was converted urban cover (Burton and Samuelson 2007). Residential and commercial property that exists on sites previously occupied by forests and grasslands can alter the watershed in multiple ways. The volume, rate and quality of surface water runoff and groundwater infiltration, quality and amount of sediment delivered to streams, the amount of light that can penetrate streams and stream temperature are examples of characteristics that can be altered by urbanization (Ryan and Packman 2005). Loss of fish habitats and more frequent flooding events are also concerns (Nelson and Booth 2002). In many parts of the country a 10% increase in impervious cover can cause noticeable stream degradation (Schoonover et al. 2005). The catastrophic effects of a local urbanization event include a fish kill downstream of Indianapolis in 1994, caused by stormwater runoff and sewer overflow (USGS 1998). Nutrient uptake in urbanized streams has been shown to decrease in a wide range of climates, from the humid Southeast to the dry Southwest (Walsh et al. 2005). Clinton and Vose suggest that major cations (K, Na, Ca, and Mg) are higher in urbanized streams than in naturally forested streams and that NO_3, NH_4 and PO_4 are at least twice as high in the urban stream than in the background forested stream. Nitrate concentrations in a stream can be decreased by the uptake and denitrification of nitrogen in the riparian zones of forests, which may be absent in urban environments (Clinton and

Vose 2005). Brett et al. 2005 state that paved urban areas can produce up to two to three times as much phosphorus as forested urban areas. Conductivity, total suspended solids (TSS) and bacteria were also highest in the urban stream.

Urbanization also leads to increased levels of trace metals, both in surface water and in river sediments. High levels of trace metals can be harmful to the local ecology and to humans. These metals can be good indicators of urbanization since their source is often industrial processes or automobile use. Metals concentrations can then be compared to background levels to determine the extent of contamination. In the case of automobile use, trace metals can either be transported by the atmosphere (wind) or deposited on the road for transport by rain into the water system. For example, Neumann et al. (2005) found that, in the Chattahoochee River, Georgia, although there were industrial sources of certain metals, urban growth was the main cause of the increase. This increase was caused by increased suburban/urban land development and automobile use, transport of more contaminated sediments from urban areas or some combination of the two. Ahmed et al (2007) and Haus et al. (2007) found that the sediments of streams located in urban areas yield higher concentrations of trace metals, specifically, cadmium, copper, nickel and zinc. These results are consistent with other research from large municipalities like Pensacola, FL, Salt Lake City, UT and Atlanta, GA (Lewis et al. 2000; Gray 2004; Rose 2002, respectively) showing that surface water runoff from extensive paved areas increases concentrations of trace metals.

Currently, no studies have been published documenting the effects of urbanization on water quality in smaller cities, especially in areas that are largely used for agriculture, like much of the Midwest. The impact of agriculture on water quality has been studied

extensively in the region, but there is little information regarding the impact that smaller cities may have. The goal of this study is to determine the seasonal effects of urbanization along the west fork of the White River in Indiana.

II. Local Setting

The study area is located in east-central Indiana in Randolph, Delaware and Madison Counties (Figure 1). The White River has its headwaters in central Randolph County and generally flows in an east-west direction within the study area. The river is part of the Mississippi River system and drains about 11,350 square miles total, in central and southern Indiana (USGS 2001) (Figure 2). Streamflow is usually highest in April or May and lowest in late summer or fall (USGS 2001). The river passes through three cities of importance in the study area. From east to west they are: Winchester with a population of 5,037, Muncie with a population of 67,430 and Anderson with a population of 59,734 (Census 2000). The study area is largely used for agriculture, mainly corn and soybean production; minor crops include wheat and hay (USDA 2007) (Table 1).

The geology of east central Indiana consists of Silurian and Ordovician carbonates near the surface with glacial till overlying the area (Figure 3). The Maquoketa Formation consists of Ordovician rocks that are composed of shale at the lower and upper parts of the formation. Rocks between the larger shale units are composed of gray dolomite with some calcareous shale (Shaver 1970). Overlying the Maquoketa is the Salamonie Dolomite. The Salamonie is Silurian in age and is characterized by three different units. The lower consists of dolomites and dolomitic limestones. The middle section is made up of dolomite. The upper part is composed of limestone and dolomite (Shaver 1970). The Silurian Waldron Formation overlies the Salamonie and is composed

of limestone and dolomitic limestone, with some oolitic shale, and is locally abundant in fossils. Overlying the Waldron is the Pleasant Mills or Louisville Limestone. The Pleasant Mills is also Silurian in age and characterized by tan to brown fine grained thick-bedded dolomitic limestone and dolomite (Shaver 1970). On top of the bedrock lies 100-200 feet of silty-clay till with thin (5-10 feet thick) sand and gravel seams (USGS 2001). These glacial sediments were deposited between 10 and 12 thousand years ago. Because of the texture of the till, surface runoff is enhanced and there is reduced recharge of groundwater.

III. Methods

Six sample sites, located up and downstream of the cities of Winchester, Muncie and Anderson were selected for study (Figure 1). The sites begin at the uppermost headwaters of the west fork of the White River and continue downstream. They were numbered WR 1 through WR 6 sequentially, beginning at the headwaters. Each city has two corresponding sites; one upstream site representing the river prior to urban influences and one downstream, representing the river after receiving urban runoff and effluents of sewage treatment plants. There were also four sample sites that were used as reference or background sites. These sites are in areas that are used for agriculture and should not be impacted by urban processes but are tributaries of the White River. They were numbered B 1 through B 4, from east to west. B 1 and B 2 are located along the Little White River, which flows into the White River between Winchester and Muncie. B 3 is located at Buck Creek, which enters the White River between Muncie and Anderson. B 4 is located on Killbuck Creek, which flows into the White River near downtown Anderson. Sites were sampled seasonally over the course of one year to include high and low flow

conditions as well as agricultural and seasonal changes. Temperature and pH were measured in the field using an Accumet® AP62 pH meter and following EPA method 150.2 (EPA 2008). Discharge data was collected online from USGS 03347000 White River at Muncie gauging station (USGS 2008) for use in constructing graphs and interpreting data.

1. Water Samples

Water samples were collected in prewashed polyethylene bottles and placed on ice until arriving at the Environmental Geochemistry Laboratory at Ball State University. Once in the lab, the samples were vacuum filtered. Samples to be measured for total suspended solids (TSS) were filtered using glass fiber filters. The filter, plus an aluminum holding tray, were weighed and recorded. The amount of river water filtered per sample was recorded in milliliters for use in TSS calculations. The particles remaining on the filter were then oven dried at 55°C for 48 hours to remove any remaining water. After drying, samples were weighed again. The weight of the filter plus the aluminum tray was subtracted from this new weight of tray, filter and particles. This value was divided by the amount of water used per sample to give TSS values in milligrams/liter (mg/L).

Samples to be analyzed for cation, anion and metals concentrations were vacuum filtered using a .45 µm membrane filter. Samples for cation and trace metals analysis were acidified to a pH<2 with trace metal grade HNO_3 to prevent precipitation. All samples were stored in a refrigerator until analysis.

Cation and anion analysis was done using a Dionex Ion Chromatograph, following EPA method 300.1 (EPA 2008). Cation and anion standards were created

using SPEX multi ion standard (Tables 2a and 2b). Standard 5 was made by direct dilution of stock solution. Standard 4 was created and used to make the remaining standard dilution series.

Cation samples were diluted at least 1:4 to ensure that concentrations fell within the standard range. Each sample was run twice with some triplicates to get better statistical analyses. Most anion samples were not diluted since collected concentrations fell within the standard range. If ionic concentrations were found to be outside the standard range, the samples were diluted further to ensure more accurate results.

Metals analysis was conducted by using an ICP-MS at Arkansas State University following EPA methods 200.2 and 200.8 (EPA 2008).

2. Sediment Samples

Sediment samples were collected twice during the sample period. Sediment was collected by grab sample using vinyl gloves to avoid contamination. It was placed in Ziploc® bags and placed in the freezer upon returning to the lab; they were also analyzed at Arkansas State University, EPA methods 200.2 and 200.8 (EPA 2008). Oxalic acid solution was used for metals extraction from the sediment. These analyses were done in July, 2008.

IV. Results

1. Total Suspended Solids

TSS results can be found in Table 4 and Figure 5. There are generally low amounts found at the headwaters (average of 7.09 mg/L). After the river passes through Winchester, TSS increases on every sample date (average of 23.31 mg/L) and never recovers to the levels measured at the headwaters throughout the course of the river. On

average there is a small increase in TSS, compared to upstream of each city, when flowing through Muncie (average of 28.04 mg/L upstream and 28.33 mg/L downstream) and Anderson (average of 24.50 mg/L upstream and 27.27 mg/L downstream).

2. pH

The pH along the White River (Table 5, Figure 6) in the study area is slightly basic with an overall range of 7.4 to 8.3 along all White River (WR) sites. The average of all sites was 8.02 with a standard deviation of 0.20. At the headwaters the average pH was 7.8 (range of 7.4 to 8.1) and increased to an average of 8.0 (range of 7.6 to 8.2) downstream of Winchester. Upstream of Muncie the average pH was 8.1 (range of 7.9 to 8.2) and decreased downstream to 8.0 (range of 7.8 to 8.3). At Anderson, the pH averaged 8.1 both upstream (range 7.8 to 8.3) and downstream (range of 7.9 to 8.3).

3. Sodium

Average sodium concentrations (Table 6, Figure 7) were calculated two different ways: first, an average that includes all sample runs (total average), and a second average does not include the last two sample runs due to the much higher concentrations (selected average). Concentrations at the uppermost headwaters range from 3.28 to 12.95 mg/L (total average of 6.90 mg/L, selected of 5.30 mg/L), while downstream of Winchester, concentrations range from 6.32 to 100.91 mg/L (total average of 32.64 mg/L, selected of 14.16 mg/L). On average, an increase of about five times the background concentration occurs as the river flows through Winchester when including all sample runs. When excluding the last two, the increase is about 2.5 times the upstream concentration. Sodium concentrations associated with the Muncie sites range from 5.21 to 18.24 mg/L (total average of 9.63 mg/L, selected of 7.22 mg/L) upstream; and from 7.50 to 153.75

mg/L (total average of 51.91 mg/L, selected of 26.82 mg/L) downstream. When considering all samples, an average increase of about five times is observed as the river flows through Muncie. When excluding the last two sample runs, an increase of 3.7 times the upstream concentration is observed. At the Anderson sites, concentrations range from 8.47 to 146.30 mg/L (total average of 46.23 mg/L, selected of 22.30 mg/L) upstream; and concentrations range from 6.79 to 111.47 mg/L (total average of 37.63 mg/L, selected of 20.10 mg/L) downstream. On average a decrease of about 19% is shown through Anderson when including all sample runs. Excluding the last two samples gives a decrease of 10%.

4. Potassium

Potassium concentrations (Table 7, Figure 8) range from 0.89 to 1.85 mg/L (average of 1.33 mg/L) at the headwaters; and from 1.36 to 5.62 mg/L (average of 2.66 mg/L) downstream of Winchester, double the upstream concentration. Potassium concentrations at the Muncie sites range from 1.35 to 2.95 mg/L (average of 2.07 mg/L) upstream; and from 1.88 to 4.41 mg/L (average of 2.79 mg/L) downstream, an increase of about 35%. Concentrations at the Anderson sites range from 1.67 to 3.70 mg/L (average of 2.57 mg/L) upstream; and from 1.67 to 3.71 mg/L (average of 2.63 mg/L) downstream, a 2% increase. All of the lowest concentrations for each site occurred during sample day 5/21/2008 while the highest concentration varied among sampling dates.

5. Calcium

Calcium concentrations (Table 8, Figure 9) range from 37.71 to 89.07 mg/L (average of 64.86 mg/L) at the headwaters and downstream of Winchester from 33.31 to

86.74 mg/L (average of 61.91 mg/L), a 5% decrease. At the Muncie sites, concentrations range from 27.86 to 65.26 mg/L (average of 50.62 mg/L) upstream; and from 31.21 to 88.49 mg/L (average of 54.92 mg/L) downstream, an increase of 11%. Calcium concentrations at the Anderson sites range from 34.69 to 91.14 mg/L (average of 57.50 mg/L) upstream; and from 28.61 to 88.45 mg/L (average of 56.11 mg/L) downstream, a decrease of about 2%. All of the lowest concentrations were on sample date 3/21/2008 and the highest concentrations were on either the 9/8/2008 or 10/27/2008 sample dates.

6. Magnesium

Magnesium concentrations (Table 9, Figure 10) follow a pattern similar to calcium. At the headwaters, concentrations range from 13.85 to 32.55 mg/L (average of 24.07 mg/L) and downstream of Winchester, from 11.69 to 35.91 mg/L (average of 23.82 mg/L), a decrease of about 1%. Upstream of Muncie, concentrations range from 9.16 to 28.29 mg/L (average of 20.83 mg/L); downstream concentrations range from 10.63 to 35.74 mg/L (average of 22.16 mg/L) an average increase of 6%. Upstream of Anderson, concentrations range from 11.54 to 34.10 mg/L (average of 22.48 mg/L) and downstream concentrations range from 11.54 to 32.47 mg/L (average of 21.38 mg/L), an average decrease of about 5%. Lowest concentrations of magnesium were on sample data 3/21/2008 and highest concentrations were on sample date 9/8/2008.

7. Bicarbonate

Bicarbonate concentrations (Table 10, Figure 11) were calculated using the program Aquachem. Concentrations at the headwaters range from 135.96 to 417.18 mg/L (average of 258.61 mg/L). Downstream of Winchester concentrations range from 124.76 to 533.97 mg/L (average of 266.76) an average increase of 3%. Upstream of

Muncie concentrations range from 104.04 to 318.27 mg/L (average of 215.87 mg/L) and downstream from 111.99 to 311.52 mg/L (average of 191.12 mg/L); a 12% decrease on average. Concentrations range from 123.97 to 301.08 mg/L (average of 200.99 mg/L) upstream of Winchester and from 100.47 to 424.81 mg/L (average of 229.20 mg/L) downstream; an average increase of 14%.

8. Chloride

Chloride concentrations (Table 11, Figure 12) at the uppermost headwaters range from 5.58 to 33.45 mg/L (average of 16.29 mg/L). Downstream of Winchester, concentrations range from 16.71 to 55.67 mg/L (average of 40.93 mg/L); a 250% increase of the upstream concentration. Chloride concentrations at the Muncie sampling sites range from 7.60 to 31.03 mg/L (average concentration of 18.85 mg/L) upstream; and from 16.51 to 59.02 mg/L (average of 34.96 mg/L) downstream, an average increase of 1.8 times the upstream concentration. Concentrations upstream of Anderson range from 15.12 to 54.6 mg/L (average concentration of 31.89 mg/L). Concentrations downstream range from 14.25 to 60.14 mg/L (average of 34.00 mg/L); a 6% increase from the upstream site.

9. Sulfate

Sulfate concentrations (Table 12, Figure 13) were calculated similarly to sodium concentrations to include all sample runs (total average) and without the last two sample runs due to the large concentrations (selected average). Total average concentrations range from 14.06 to 41.82 mg/L at the uppermost site (average of 27.88 mg/L) to 12.98 to 81.34 mg/L (average 39.66 mg/L) downstream of Winchester, a 42% increase from the upstream site. Selected average concentrations range from 14.06 to 32.93 mg/L at the

uppermost site (average of 25.23 mg/L) to 12.98 to 38.72 mg/L (average of 28.14 mg/L) downstream, an 11% increase from the upstream site. At the Muncie sites, concentrations range from 14.44 to 45.87 mg/L (average concentration of 32.09 mg/L) upstream; and from 19.31 to 390.03 mg/L (average of 136.95 mg/L) downstream, an average increase of over four times the upstream concentration. Upstream of Anderson, concentrations range from 23.49 to 392.22 mg/L (average of 130.87 mg/L). Downstream, concentrations range from 14.95 to 251.43 mg/L (average of 81.50 mg/L); a 38% decrease from the average upstream concentration.

10. Nitrate

Nitrate concentrations (Table 13, Figure 14) upstream of Winchester range from 0.34 to 55.98 mg/L (average of 16.90 mg/L and median of 15.50 mg/L). Downstream concentrations range from 3.94 to 29.31 mg/L (average of 11.42 mg/L) which is a decrease of 33% the upstream concentration. At the Muncie sites concentrations range from 0.30 to 22.75 mg/L (average of 7.39 mg/L) upstream; and from 4.21 to 16.29 mg/L (average of 9.73 mg/L) downstream, a 31% increase from the upstream site. Upstream of Anderson, concentrations range from 3.95 to 17.83 mg/L (average of 9.09 mg/L). Downstream, concentrations range from 3.14 to 14.10 mg/L (average of 8.10 mg/L), an 11% decrease from the upstream concentrations.

11. Trace Metals

Sediment used to calculate trace metals concentrations was collected on two different sampling dates, 5/9/2008 and 7/2/2008. However, only the 5/9/2008 sample date results are accurate due to an error in collection or analyzing procedure. Full trace metals results can be found in Table 14.

11.a. Cadmium

Cadmium concentrations (average of Cd 111 and Cd 114) can be found in Table 15. At WR1 the concentration is 0.0055 mg/kg and after the river passes through Winchester, the concentration increases slightly to 0.0058 mg/kg. At the sites around Muncie, the concentration increases from 0.0059 mg/kg upstream to 0.0114 mg/kg downstream; an increase of almost twice the upstream concentration. Upstream of Anderson, cadmium concentration has recovered to 0.0037 mg/kg but increases about four times to 0.0155 mg/kg.

11.b. Chromium

Chromium concentrations (average of Cr 52 and Cr 53) can be found in Table 16. Upstream of Winchester, the measured chromium concentration is 0.75 mg/kg and increases about 60% to 1.21 mg/kg downstream. In Muncie, the concentration increases from 0.97 mg/kg upstream to 2.30 mg/kg downstream, an increase of twice the upstream concentration. At Anderson, concentrations increase from 1.03 mg/kg to 6.98 mg/kg as the river flows through the city; an increase close to seven times the upstream concentration.

11.c. Copper

Copper concentrations (average of Cu 63 and Cu 65) can be found in Table 17. Copper concentrations increase through Winchester from an upstream concentration of 4.08 mg/kg to a downstream concentration of 10.85 mg/kg; roughly a 200% increase of the upstream concentration. Concentrations recover before Muncie, with an upstream concentration of 7.28 mg/kg but increase to 16.78 mg/kg downstream; again, an increase of about twice the upstream concentration. Upstream of Anderson, the copper

concentration is 3.01 mg/kg but increases close to seven times the upstream concentration to 20.56 mg/kg.

11.d. Nickel

Nickel concentrations (average of Ni 60 and Ni 62) can be found in Table 18. Upstream of Winchester, the average nickel concentration equaled 1.84 mg/kg. This concentration almost doubles to 3.30 mg/kg downstream of the city. At Muncie, the concentration upstream is 2.99 mg/kg and increases to 3.66 mg/kg downstream; a 23% percent increase. Upstream of Anderson, the concentration drops to 0.98 mg/kg but, after the river passes through the city, increases to 6.12 mg/kg downstream; a six fold increase.

11.e. Tin

Tin concentrations can be found in Table 19. At the headwaters, the tin concentration equaled 0.07 mg/kg. After the river passes through Winchester, the tin concentration increases to 0.41 mg/kg, an increase of six times the upstream concentration. Upstream of Muncie, the concentration dropped to 0.27 mg/kg but increased over three times the upstream concentration to 1.04 mg/kg. As the river flows through Anderson, the concentration increases from 0.18 mg/kg upstream to 0.60 mg/kg downstream, an increase of over three times.

11.f. Zinc

Zinc concentrations are found in Table 20. The zinc concentration at the headwaters equaled 4.52 mg/kg. After the river passes through Winchester, the zinc concentration increases to 13.07 mg/kg, an increase of close to three times the upstream concentration. Upstream of Muncie, the concentration dropped to 7.22 mg/kg but increased to four times the upstream concentration to 28.93 mg/kg downstream of

Muncie. As the river flows through Anderson, the concentration increases from an upstream concentration of 8.41 mg/kg to a downstream concentration of 37.90 mg/kg, over a fourfold increase.

V. Discussion

Results show that as the White River passes through Winchester, Muncie and Anderson pH, TSS and the chemistry of the river is changed. There are noticeable changes in major ionic concentration that are associated with urbanization, including sodium, potassium, chloride, sulfate and in certain conditions, nitrate. Other changes in ionic concentration are attributed to geologic or agricultural factors.

1. Temperature

Temperature was recorded for completeness (Table 3, Figure 24) but does not have any impact on the concentration of cations and anions or on the solubility of these ions. Some studies (Clinton and Vose 2005) suggest temperature may increase in urban area. In this study there is no evidence of this occurring. The increases in overall temperature occur due to daily warming, as each sample site was sampled in the same order every time as the air temperature increased.

2. Total Suspended Solids

Total suspended solids measures the amount of particles suspended in the water column. During storm flow events, more particles are washed into the river, thus increasing the amount of particles in the water column. In urban areas, the amount of TSS usually increases due to the appearance of impearmeable cover delivering runoff to the river more efficiently (Clinton and Vose 2005; Nelson and Booth 2002). This process is the cause of the increases in TSS during precipitation events in this study (Figure 5).

On sample dates 3/21/2008, 5/9/2008 and 6/9/2008 high amounts of TSS were measured and attributed to precipitation and runoff since these samples were collected following a rainfall event. On all three of these sample dates, TSS at least doubles when the river flows through the city of Winchester. Downstream of Muncie and Anderson, TSS data is not as consistent on these sample dates, with only increases on 3/21/2008 through Muncie and 6/9/2008 through Anderson. Evidence of other factors contributing to the amount of TSS, especially during low flow events, includes output from sewage treatment plants. For example, samples collected on 7/2/2008 were collected during the lowest flow of the study period and showed increasing TSS values downstream of Winchester and Anderson, however there was no precipitation event causing runoff, the source is likely discharge from local sewage treatment plants.

3. pH

Values for pH are dependent on many factors including geology, discharge and urbanization (Table 4, Figure 6). The geology of the study area is composed of carbonate rocks. Water in contact with these rocks, under normal atmospheric CO_2 pressure, is slightly basic (Drever 1997; Langmuir 1997), as shown in this study. During periods of low flow this relationship is evident as the water flowing into the White River has been in contact with the subsurface geology for a longer period of time. The pH of the background samples taken on 5/9/2008 and 7/2/2008, show values that are similar to those taken along the White River (Figure 6b). The pH at B 2 (7.95 on 5/9/2008 and 8.17 on 7/2/2008), which is located between WR 2 and WR 3, is between the pH observed in Winchester and Muncie. During periods of high or storm flow the pH decreases. Dilution of baseflow and less residence time with bedrock causes the water to be slightly

less basic. Samples taken on 3/21/2008, 5/9/2008 and 6/9/2008 show the lowest pH values overall, and were observed on the three days with the highest flow. Previous studies (Clinton and Vose 2005; Rose 2002) suggest that urbanization may be a factor that affects pH. Clinton and Vose (2005) found that pH was consistently higher in their selected urbanized stream than in the background or forested stream. Rose (2002) suggests that dilution with slightly acidic street runoff is responsible for lowering the pH in urbanized watersheds. Both of these studies were conducted in different geologic provinces, the Piedmont and Blue Ridge respectively, which contain igneous and metamorphic rocks that are not present in the White River basin. The pH values in this study suggest that the bedrock geology of carbonates and dilution from rainwater are the two main factors affecting the pH along the White River. On average, the pH increases on every sample date through Winchester (pH +0.20 from upstream site) and on all but three sample dates through Anderson (pH +0.03 from upstream site) but decreases through Muncie (pH -0.10 from upstream site) on every sample date. In this study area it does not appear that cities have a consistent impact on the pH.

4. Ion-Discharge and Ion-Ion Correlation

Discharge data for the White River at Muncie is available online from USGS 03347000 White River at Muncie gauging station (USGS 2008) (Figure 4). The discharge data were used to define the relationship between river chemistry and discharge. The goal was to see how much the chemistry of the river was impacted by dilution and rock-water interactions. There is no gauging station at Winchester and there was no discharge data available from the Anderson gauging station, so the Muncie gauging station was used to serve as a proxy to determine the relationship between ionic concentration and

discharge at the headwaters site. The data used in this work is still considered provisional, so it has not received final approval from the USGS. There is also a gap in the discharge data from 7/19/2008 to 8/11/2008. The source of this gap is not known.

4.a. Winchester

An ion-discharge correlation was constructed for the uppermost headwaters site, WR 1, using the Muncie gauging station levels (Figure 16a). The graph suggests that for all values of discharge, bicarbonate and calcium are the dominant ionic species. Calcium and bicarbonate are expected to be the dominant species in the river at this point due to the local geology (carbonates), pH (average of 7.8), and the lack of a source for other ions. Gypsum is not a sufficient source of sulfate, as the relationship between Ca and SO_4 is exponential with an r^2= 0.50 (Figure 17). The exception is the nitrate concentration on 5/9/2008 which is higher than calcium concentration. Given the month, this increase is due to the application of nitrate-rich fertilizers during the spring planting period and also confirmed by higher nitrate concentrations along background sites (agricultural areas) on this sampling date (Figure 15a). None of the background site concentrations of nitrate are as high as 55.99 mg/L seen at WR 1. High nitrate concentrations at WR 1 are significant because they mask any potential inputs from urban areas. Even with input from tributaries, concentrations are high enough that as the river flows through the cities, nitrate increases caused by urbanization are small compared to the already high agricultural inputs. Since the river has not passed through any urbanized areas at WR 1, and there are only lightly used roads in the area, the chemistry of the water is controlled by local geologic input and, during certain times of the year, the application of fertilizers.

Downstream of Winchester, at WR 2, the concentration of major cations and anions, associated with urbanization, has increased. Sodium, potassium and chloride concentrations (Figures 7, 8 and 12 respectively) increase on every sample date. Sulfate concentrations also increase on every date except 3/21/2008 (Figure 13). Winchester contributes a large amount of sodium and chloride for a city of its size with a population of 5,037 (2000 Census), potassium levels increase as well. On average the amount of sodium increases significantly (up to 8 times the upstream concentration) as the river passes through Winchester (Figure 7). This increase correlates with an increase (up to 9 times the upstream concentration) in chloride concentration as well (Figure 12). Graphically these two ions tend to follow a similar pattern and there is a strong linear correlation with an *r2*= 0.91 using all sample dates except that last two and an r^2=0.99 when using just 9/8/2008 and 10/27/2008 (Figure 20b). Increases occur during both high and low flow, but overall concentration is lower during periods of high flow, suggesting that dilution is affecting the concentration.

Other studies (Rose 2002) suggest that urbanization can increase the levels of calcium, magnesium and bicarbonate by the dissolution of pavement. On average calcium, magnesium and bicarbonate concentrations decrease slightly throughout the course of the river. The decrease of calcium and magnesium indicates that Winchester is either too small and/or the concentration in the river is still being controlled by local geology. Bicarbonate concentration also closely mimics the pattern of the calcium and magnesium as it is the primary anion created by the dissolution of calcite, in the pH range found in the study area (Drever 1997). However on sample dates 9/8/2008 and 10/27/2008, magnesium and bicarbonate increase. The cause of the increase during

periods of low flow that also correspond to a decrease in calcium concentration is unknown.

Increased nitrate concentration can be caused by urbanization. In and around Winchester the land use is largely agricultural, which can mask any potential input from urban sources during most of the year. A decrease in nitrate concentration can be caused by denitrification and uptake by biota. If this is greater than the amount being supplied by sewage, than an overall decrease in nitrate concentration will be seen. Results suggest however, that during non-fertilizing months, there is an increase in nitrate concentration that is likely caused by urbanization. Clinton and Vose (2005) suggest that nitrate concentrations in their study area (the upper Chattooga River watershed in western North Carolina) are higher in urbanized areas, caused by non-point sources such as septic drain fields and potentially fluctuating discharge from local waste water treatment plants. When Clinton and Vose (2005) compared nitrate concentrations in the urbanized area to the nitrate concentrations of their reference streams (sites were often in National Forests), the urbanized area had higher concentrations. In this study area along the White River, there is evidence of nitrate input from urbanizing factors (leaking septic systems or fluctuations in discharge of sewage treatment plants), but this input is small compared to concentrations already found in the uppermost headwaters and background sites (fertilizers and animal wastes). The background sites are in areas mostly used for agriculture, so there is active application of nitrate in the form of fertilizer, so it is expected that there are higher concentrations of nitrate compared to levels found in an undisturbed forest because input is greater than uptake. Walsh et al. (2005) suggest that nitrate concentrations are higher in urbanized areas because of the removal of the riparian

zone which would prevent uptake by biota. This would contribute to the elevated levels of nitrate observed as the river passes through Winchester during the fall sampling dates since biota cannot actively remove nitrate from the water. The 9/8/2008 and 10/27/2008 sample dates indicate a considerable increase in nitrate concentration as the river flows through the city of Winchester. Since these sampling dates occur during periods of low flow in the fall, the likely cause of increased nitrate concentration is urbanization from sewage.

Sulfate concentration also increases minimally (up to 2.5 times upstream concentration) when compared to the increases seen in sodium and chloride concentrations (Figure 13). This suggests that Winchester does not contribute much sulfate to the White River. With the exception of the last two sample dates, there is only a minimal increase in sulfate concentration and there is a decrease on 3/21/2008, the highest discharge of the study period.

Trace metal concentrations in the sediment of the White River are also shown to have been impacted by urban processes (Figure 22). The increases of several trace metals, including cadmium, chromium, copper, nickel, tin and zinc, commonly associated with urban sources can be seen. Winchester is a small city with very little industry and road traffic, so increases in trace metals will stand out in comparison to headwaters/background concentrations that show rural levels. Ahmed (2007) suggests that zinc contamination in the shallow surface is due to either industrial output or from automobile traffic. Due to the limited industry in Winchester, it can be concluded that the elevated zinc levels found downstream of Winchester are primarily caused by the abrasion of tires that is then washed into the river. The appearance of chromium and

nickel in sediments can be caused by the weathering of crystalline (igneous) rocks, as suggested by Sindern et al. (2007). In the White River basin, however, there are no igneous rocks near the surface suggesting the source of increased chromium and nickel is urban in nature, most likely from automobiles.

4.b. Muncie

Ion-discharge correlations were constructed at WR 3 for comparison (Figure 16b) with WR 4. Calcium and bicarbonate are the dominant ions for all discharge values, even during periods of low flow. The shape of the graph is similar to that of the graph at WR 1. The increases observed as the river flows through Winchester have been lowered to near background levels. Dilution by tributaries and nutrient uptake by biota allows the river to "recover" before it reaches Muncie.

Average sodium, potassium and chloride concentrations have fallen by 60%, 23% and 54% respectively from WR 2 to WR 3. This can be attributed to the input from the Little White River (B 2). Background samples (Figures 15a, b) show that the concentrations of these three ions, in the background/rural setting, help to lower the concentrations much closer to the headwaters concentration.

Calcium, magnesium and bicarbonate concentrations have dropped minimally to concentrations similar to those found at B 2, just upstream of where the Little White River enters the White River.

Sulfate concentrations between WR 2 and WR 3 decrease in samples of low discharge and increase in samples of high discharge. This data indicates that sulfate concentrations along this part of the White River are controlled by the amount of precipitation and runoff that flows into the river. Background samples taken on 5/9/2008

(high flow) and 7/2/2008 (low flow), show concentrations of sulfate that illustrate this point. During high flow, the background sample at B 2 has a concentration (18.12 mg/L), almost identical to the concentration downstream of Winchester (18.11 mg/L) but at WR 3, an overall increase (19.39 mg/L) is observed. During low flow, B 2 has a concentration (28.90 mg/L) that is lower than what is seen downstream of Winchester (34.99 mg/L) and close to WR 3 (28.01 mg/L).

Nitrate concentrations decrease in every sample between WR 2 and WR 3. This suggests that in this area, uptake is greater than the input of nitrate. The only exception is sample date 5/9/2008, which shows very high levels of nitrate due to the application of fertilizers. During the planting season the impact from fertilizing is greater than the amount of uptake and allows for increases in nitrate concentration to be seen.

Trace metals associated with urbanization have also dropped to near background levels at WR 3. Trace metals adsorb to the surface of sediments, thus making their transport long distances downstream difficult. Since the trace metals analyzed in this study are found in automobile pollution, the closer to a higher traveled road the sample site, the higher the concentration of trace metals is likely to be. The road near B 1 is much less traveled than B 2 and so not unexpectedly the concentration of trace metals (except tin) is higher at B 2. In the case of nickel, B 2 concentration is higher than WR 3 suggesting that even with the input from the Little White River the distance between B 2 and WR 3 and between WR 2 and WR 3 is large enough to return the river to background levels before it reaches Muncie.

Discharge-concentration correlations could most accurately be constructed from data at WR 4 because the Muncie Gauging station is downstream of Muncie. During

periods of high flow calcium is the dominant ion (Figure 16c). However, during periods of low flow sodium and sulfate become the dominant ions. Ion-discharge correlations for sodium, calcium, magnesium, chloride and sulfate were found to be exponential with r^2 values equal to 0.69, 0.96, 0.95, 0.72 and 0.74 respectively (Figures 18a-e). These values do not include the last two sample runs of 9/8/2008 and 10/27/2008 because the concentrations of ions on these two dates is believed to be controlled by another factor, perhaps precipitation flushing the soil of elevated levels of ions that collected during the dry season. When including the ionic concentrations on these two sample dates the r^2 values drop for sodium, calcium, magnesium, chloride and sulfate to 0.58, 0.85, 0.83, 0.21 and 0.62 respectively (not pictured). Potassium and nitrate have poor relationships with discharge producing polynomial r^2 values equal to 0.02 and 0.19 respectively. This data indicates that potassium and nitrate are not strongly tied to discharge and are more dependent on other factors such as the seasonal application of fertilizers and, in the case of nitrate, sewage discharge.

Calcium, magnesium and bicarbonate contribution to the river downstream of Muncie has changed. The strong relationship between calcium and magnesium is caused by the local limestone and dolostone. Taking into account all sample sites the relationship is linear with an r^2= 0.93 (Figure 19), with almost three times as much calcium than magnesium on average. Low discharge in the White River basin indicates periods of less rainfall and less surface runoff to the river. The graph of discharge, and its relationship with calcium and magnesium (Figures 18 b, c), indicates that during periods of low flow, overall calcium and magnesium concentrations are higher. This is due to water-rock interaction, residence time and surface runoff. During periods of low

flow, ground and interflow contribute most of the water to the river, with little surface runoff. The water is in contact with shallow and subsurface geology, causing the chemistry of the water to resemble the chemistry of the rocks themselves. When there is more rainfall, surface runoff and discharge are higher causing overall calcium and magnesium concentrations to decrease because there is very limited contact with underlying geology and more surface runoff. However, there is a slight increase in calcium and magnesium concentrations as the river flows through Muncie. During periods of high flow there is also an increase in the amount of bicarbonate, as well. Increased levels of bicarbonate, during periods of increased precipitation, suggest that the source of the increase is the dissolution of pavement. Previous studies (Rose 2002) have suggested that urbanization may increase the concentration of calcium and bicarbonate in rivers by the dissolution of cement. In this study, there is evidence of that occurring after the river flows through Muncie only, while in Winchester and Anderson calcium concentrations are lower downstream. This illustrates that the calcium, magnesium and bicarbonate concentrations in the White River are dominated by the dissolution of calcite from the local bedrock, but Muncie itself does contribute to the total concentration.

Sodium, chloride and sulfate are also exponentially related to discharge (Figures 16 a, d, e). There is not a significant natural source of these ions so the increased concentrations found in the White River must be attributed to urbanization in the form of runoff and sewage discharge. To examine the relationship between these ions, correlation graphs of Na-Cl and Na-SO_4 were constructed. The relationship between Na-Cl is expected to be strong. When looking at all six sample sites, a linear correlation is present with r^2= 0.63 (Figure 20a). There is a strong Na-Cl correlation upstream of Muncie, r^2=

0.91(Figure 20b), while the data downstream of Muncie and Anderson only gives an r^2= 0.62 (Figure 20c). These data suggest that upstream of Muncie, most of the sodium and chloride that enters the White River is in the form of Na-Cl, but downstream there are other sources of the ions. Rose (2002) suggests that higher sodium and chloride concentrations could be the product of evaporate minerals left after rainfall in the shallow subsurface. This interpretation could be applied in this study for the last two sampling dates (9/8/2008 and 11/27/2008). A dry period followed by a rain event to dissolve and flush the accumulations of ions, could explain the dramatic increases seen in sodium and chloride in early fall. Samples should not have been affected by salt application after snowfall since no samples were taken during the peak of the winter.

The Na-SO_4 relationship was also examined. When plotting all six sample sites, a linear correlation is present with r^2= 0.92 (Figure 21a). Plotting just the first three sites (upstream of Muncie) gives a very weak linear correlation with r^2= 0.36 (Figure 21b), while correlating the concentrations downstream of Muncie gives a correlation with r^2= 0.98 (Figure 21c). This suggests that upstream of Muncie, sodium and sulfate are entering the river at least partially independently, but downstream of Muncie the two are entering the river as Na-SO_4. Sulfate concentrations during the last two sample runs were also very high and may also be the product of the flushing of dissolved salts after a dry period.

Trace metals that are associated with urbanization are also shown to increase (Figure 22). Unlike Winchester, there is industry in Muncie and so the source of the increase could be caused by automobile use and industrial processes. The six trace

metals that were examined because of their characteristics as urban contamination, all show increases in concentration downstream of Muncie.

4.c. Anderson

Upstream of Anderson, at WR 5, the impacts from the city of Muncie are still observed in White River geochemistry. The streams that flow into the White River between Muncie and Anderson (Buck Creek and Killbuck Creek, sites B 3 and B 4, respectively) do not dilute the water back down to near background levels (as was the case with tributaries between Winchester and Muncie). This means that downstream of Muncie the chemistry of the river is permanently altered and does not recover to headwaters/background levels again.

Average sodium, potassium, chloride and sulfate concentrations have dropped minimally between WR 4 and WR 5 (11%, 8%, 9% and 5% respectively). Contribution from Buck Creek (B 3) helps to lower the concentrations upstream of Anderson, but not significantly. For example, concentrations of these ions in Buck Creek entering the White River downstream of the mouth of B 3 on 7/2/2008 (8.37 mg/L, 1.38 mg/L, 25.35 mg/L and 44.85 mg/L, respectively), are lower than the concentrations observed at WR 4 (35.59 mg/L, 2.24 mg/L, 37.82 mg/L and 112.32 mg/L, respectively). This contribution helps to lower the ionic concentrations at WR 5 (27.55 mg/L, 1.91 mg/L, 35.76 mg/L and 83.39 mg/L, respectively) but is not a large enough contribution to lower concentrations to background levels.

Average calcium, magnesium and bicarbonate concentrations show a small increase in concentration. The likely source is water flowing into the White River from the larger tributary of Buck Creek (B 3). For example on sample date 7/2/2008, calcium

and magnesium concentrations at B 3 are 72.39 mg/L and 23.93 mg/L, respectively. The concentrations of the two cations at WR 5 is 64.05 mg/L (an increase from 61.56 mg/L at WR 4) and 21.99 mg/L (an increase from 21.67 mg/L at WR 4). Bicarbonate concentration increases from 188.60 mg/L at WR 4 to 206.45 mg/L at WR 5 on this same sampling date (7/2/2008). This tributary is believed to be mostly unaffected by urbanization and brings a large amount of calcium-magnesium-bicarbonate rich water into the river.

Nitrate concentration at WR 5 is lower than at WR 4. The only exceptions are on 5/9/2008 and 6/9/2008. As previously mentioned, the increase in nitrate on 5/9/2008 is due to fertilizing in the study area. On this sample date, B 3 shows higher concentrations than either WR 4 or WR 5 suggesting that Buck Creek is loading the White River with nitrate. The increase on 6/9/2008 is somewhat unexpected. It is a high discharge sample, so it is possible that there may have been some fertilizing still ongoing at this time.

Trace metals drop significantly between WR 4 and WR 5. The low concentrations that are coming into the White River (Buck Creek), combined with the limited mobility in general suggests that, like Winchester to Muncie, concentrations of trace metals in sediment drop to near background levels. It is interesting to note that the concentrations of the six trace metals indicative of urbanization have fallen to pre-Muncie concentrations, with the exception of chromium.

Downstream of Anderson, at WR 6, TSS, pH, cation and anion data are inconclusive. Overall it appears that the large increases of certain ions, mainly sodium, sulfate and to a lesser extent, chloride, from Muncie are still showing downstream of Anderson and are masking any input from Anderson itself. It is also possible that the

input from Killbuck Creek (B 4) is masking any increases. Unlike other tributaries that meet the White River outside of the cities, Killbuck Creek flows into the White River in downtown Anderson so there is already dilution before the river reaches WR 6. On both 5/9/2008 and 7/2/2008, sodium (9.25 and 10.55 mg/L), chloride (31.31 and 32.03 mg/L) and sulfate (25.67 and 42.87 mg/L) concentrations from Killbuck Creek (B 4) are lower than the concentration at WR 6. This suggests that even though there are increases in concentration of sodium and sulfate from WR 5 to WR 6, on 5/9/2008 for example, the input from Killbuck Creek is causing the apparent increase to be less, by diluting the White River.

Perhaps the best indicator of urban impact on the river at Anderson is trace metals concentrations. The six trace metals that are specified because of their appearance in automobiles and industry are shown to increase. In fact the trace metals more than triple through Anderson, and achieve higher concentrations than those found in background/upstream samples. Cadmium, chromium, copper, nickel, tin and zinc show dramatic increases downstream of Anderson (418%, 678%, 683%, 624%, 333% and 451%, respectively). Input from industrial wastes as well as automobile pollution in an urban setting contribute to the observed concentrations.

Trace metals concentrations from Killbuck Creek, except tin, are the highest among the other background samples, presumably because the road at the sample site is more heavily traveled. Concentrations of cadmium, chromium, copper, nickel, and zinc (0.0132 mg/kg, 1.40 mg/kg, 7.98 mg/kg, 4.40 mg/kg and 24.97 mg/kg, respectively) in sediments of Killbuck Creek are higher than the concentrations at WR 5 (0.00371 mg/kg, 1.03 mg/kg, 3.01 mg/kg, 0.98 mg/kg and 8.41 mg/kg, respectively) so there is less

dilution and Killbuck Creek appears to be contributing to the total trace metals concentrations as opposed to lowering to background levels. As mentioned previously, Killbuck Creek flows into the White River in downtown Anderson.

5. Computer Modeling

Aquachem® was used to calculate bicarbonate concentration but also to create a Piper diagram (Figure 23), determine water type at each sample site (Table 21) and to calculate the saturation indices with respect to calcite (Table 22). This was done to analyze the impact urbanization has on river chemistry as a whole. The Piper Diagram shows that for cations, the ratio of calcium and magnesium stays about the same during the course of the river in the study area but the ratio of sodium increases. This means that sodium is not replacing calcium or magnesium in the water but being added to the total amount of cations. For anions, bicarbonate dominates the samples upstream of Winchester and Muncie. Downstream of these cities and Anderson, chloride and sulfate become more dominant.

Water type (Table 21) overall is characterized by Ca-Mg-HCO_3 with other ions like Na, Cl, SO_4 and NO_3 also present. Upstream of Winchester, water type is generally Ca-Mg-HCO_3, characteristic of natural waters in a calcite rich setting. The exception is sample date 5/9/2008, which has high nitrate concentrations due to fertilizing and a water type of Ca-Mg-HCO_3-NO_3. After the river flows through Winchester, the increases of Na and Cl are enough to change the water type to include these ions, except on sample dates 3/21/2008 and 6/9/2008 which remain as Ca-Mg-HCO_3 due to higher discharge and dilution of any Na and Cl washed into the river. Upstream of Muncie, the water types have all returned to Ca-Mg-HCO_3, indicating that, in terms of major ions, the river has

recovered to its natural type by dilution. Downstream of Muncie, Na, Cl and SO_4 have increased enough to be included in the water type except on sample dates 3/21/2008 and 6/9/2008, again due to increased discharge and dilution. Upstream of Anderson, water type has, except on high flow sample dates, not recovered to natural levels and still shows Na, Cl and SO_4 as major ions. Downstream of Anderson, water type still includes Na, Cl and SO_4 and most likely is permanently altered. Sample dates 3/21/2008 and 6/9/2008 were taken during periods of high discharge and the water type (Ca-Mg-HCO_3) does not change during the course of the river. During periods of higher discharge, dilution is responsible for the generally lower concentrations of ions Na, Cl and SO_4. This can be seen in the water type analysis and verified by the graphs of ionic concentrations (Figures 7, 12 and 13).

Saturation indices (SI) (Table 22) indicate that the river is saturated with respect to calcite except on all sites sampled on 3/21/2008 (highest discharge) and the Muncie sites (WR 3 and WR 4) on 5/9/2008. The saturation indices for calcite indicate that dissolution has reached its largest and that more calcite cannot dissolve, even with longer residence time. SI can also be used to examine the relationship with White River pH. The lower the SI, the lower the pH tends to be. For example during the sample dates with the highest discharge (Figure 4; 3/21/2008, 5/9/2008 and 6/9/2008) the SI values are low, or in the case of 3/21/2008, negative (undersaturated). This corresponds to lower pH values (Figure 6) on these dates. The higher discharge is attributed to runoff caused by precipitation, causing there to be less residence time and less dissolution of calcite.

VI. Conclusions

The cities of Winchester, Muncie and Anderson are impacting the water quality of the White River despite the river being located in a largely agricultural area. The pH, TSS, major cations and anions and trace metals in sediments are all shown to be impacted by these cities. Even the small city of Winchester (pop. 5,037 as of 2000 Census) causes considerable increases in the TSS and chemistry. Many studies (Clinton and Vose, 2005; Leung et al., 2005; Rose 2002; Schoonover et al., 2005; Neumann et al. 2005, Ahmed; 2007) have shown that major cation and anion and trace metals concentrations increase in urbanized watersheds. The results of this White River study are consistent with others that have been conducted in larger cities. The differences in geology and land use outside of the urban areas cause differences in the data among the studies. Sodium and sulfate concentrations on sample dates 9/8/2008 and 10/27/200 are dramatically higher than during any previous sampling date on the downstream side of Winchester and Muncie and chloride is higher downstream of Winchester. There are no known catastrophic events that would have released such elevated levels of sodium, chloride and sulfate into the river. One possible explanation is that, since these samples were collected during base flow, these ions accumulated as salts in the shallow subsurface. During the next precipitation event, there was a washing and dissolving of these salts into the river. The occurrence of such high levels of sulfate and its strong correlation with sodium is unexpected. Water softeners are used in private residences to soften the water in the area. Most water softeners work by an ion-exchange membrane, often causing sodium ions to be replaced by calcium ions on the membrane, thus causing elevated levels of sodium in the water system. Other possible explanations include the use of sulfate in the treatment

of waste water at the Muncie Sewage treatment plant, dissolution of fly ash from pavement (Rose 2002) and coal burning at power plants.

VII. References

Ahmed, Faruque; Bibi, M. Hawa; Ishiga, Hiroaki; 2007. Environmental assessment of Dhaka City (Bangladesh) based on trace metal contents in road dusts. Environmental Geology 51; 975-985.

Brett, Michael T.; Arhonditsis, George B.; Mueller, Sara E.; Hartley, David M.; Frodge, Jonathan D.; Funke, David E.; 2005. Non-Point-Source Impacts on Stream Nutrient Concentrations Along a Forest to Urban Gradient. Environmental Management 35(3); 330-342.

Burton, Michele L. and Samuelson, Lisa J.; 2007. Influence of urbanization on riparian forest diversity and structure in the Georgia Piedmont, US. Plant Ecology 195; 99-115.

Clinton, Barton D. and Vose, James M.; 2006. Variation in stream water quality in an urban headwater stream in the Southern Appalachians. Water, Air, and Soil Pollution 169; 331-353.

Drever, James. The Geochemistry of Natural Waters, Third Edition. Prentice-Hall, Inc. New Jersey, 1997.

Gray, L.; 2004. Changes in water quality and macroinvertebrate communities resulting from urban stormflows in the Provo River, Utah, USA. Hydrobiologia 518; 33-46.

Haus, N.; Zimmerman, S.; Wiegand, J.; Sures, B.; 2007. Occurrence of platinum and additional traffic related heavy metals in sediments and biota. Chemosphere 66; 619-629.

Langmuir, Donald. Aqueous Environmental Geochemistry. Prentice-Hall, Inc. New Jersey, 1997.

Leung, Chi-man; Jiao, Jiu J.; Malpas, John; Chan, Wing-tat; Wang, Yan-xin; 2005. Factors affecting the groundwater chemistry in a highly urbanized coastal area in Hong Kong: an example from the Mid-Levels area. Environmental Geology 48; 480-495.

Lewis, Michael A.; Moore, James C.; Goodman, Larry R.; Patrick, James M.; Stanley, Roman S., Roush, Thomas H.; Quarles, Robert L.; 2001. The effects of urbanization on the chemical quality of three tidal bayous in the Gulf of Mexico. Water, Air, and Soil Pollution 127; 65-91.

Nelson, Erin J. and Booth, Derek B; 2002. Sediment sources in an urbanizing, mixed land-use watershed. Journal of Hydrology 264; 51-68.

Neumann, Klaus; Lyons, W. Berry; Graham, Elizabeth Y.; Callender, Edward; 2005. Historical backcasting of metal concentrations in the Chattahoochee River, Georgia: Population growth and environmental policy. Applied Geochemistry 20; 2315-2324.

Ryan, Robert J. and Packman, Aaron I.; 2006. Changes in streambed sediment characteristics and solute transport in the headwaters of Valley Creek, an urbanizing watershed. Journal of Hydrology 323; 74-91.

Rose, S.; 2002. Comparative major ion geochemistry of Piedmont streams in the Atlanta, Georgia region: possible effects of urbanization. Environmental Geology 42; 102-113.

Schoonover, Jon E.; Lockaby, B. Graeme; Pan, S; 2005. Changes in chemical and physical properties of stream water across an urban-rural gradient in western Georgia. Urban Ecosystems 8; 107-124.

Shaver, Robert H.; Burger, Ann M.; Gates, Gary R.; Gray, Henry H.; Hutchison, Harold C.; Keller, Stanley J.; Patton, John B.; Rexroad, Carl B.; Smith, Ned M.; Wayne, William J.; Wier, Charles E.; 1970. Compendium of Rock-Unit Stratigraphy in Indiana. Indiana Geological Survey 43.

Sindern, S.; Lima, R.; Schwarzbauer, J.; Petta, R.; 2007. Anthropogenic heavy metal signatures for the fast growing urban area of Natal (NE-Brazil). Environmental Geology 52; 731-737.

United States Census Bureau, 2004. Census Data for the state of Indiana. http://www.census.gov/census2000/states/in.html.

United States Department of Agriculture, 2007. http://www.nass.usda.gov/Statistics_by_State/Indiana/Publications/County_Estimates/cebeans.asp.

United State Environmental Protection Agency, 2008. Clean Water Act Analytical Test Methods. http://www.epa.gov/waterscience/methods/method/index.html.

United States Geological Survey, 2008. Real-Time Water data for White River at Muncie, IN. http://waterdata.usgs.gov/nwis/uv?03347000.

United States Geological Survey, 2001. Brief Description of the White River Basin. http://in.water.usgs.gov/nawqa/wr00002.htm.

United States Geological Survey, 1998. Circular 1150: Water Quality in the White River Basin; Indiana, 1992-1996.

Walsh, Christopher J.; Roy, Allison H.; Feminella, Jack W.; Cottingham, Peter D.; Groffman, Peter M.; Morgan II, Raymond P.; 2005. The urban stream syndrome: current knowledge and the search for a cure. Journal of the North American Benthological Society 24(3); 706-723.

Table 1. Corn and Soybean production in thousands of acres (USDA 2007).

County	**Corn**		**Soybeans**	
	Planted	**Harvested**	**Planted**	**Harvested**
Randolph	88.3	87.7	108.3	108.1
Delaware	62.9	61.8	88.3	88.2
Madison	80.5	79.3	98.6	98.6

Table 2a. Cation standard specifications.

SPEX			Li	Na	K	Mg	Ca	NH4
Stock Solution		mg/L	50	200	200	200	1000	400
Standard 5	1:20 SPEX	1:20 SPEX	2.5	10	10	10	50	20
Standard 4	1:100 SPEX	1:100 SPEX (B)	0.5	2	2	2	10	4
Standard 3	1:400 SPEX	1:4 B	0.125	0.5	0.5	0.5	2.5	1
Standard 2	1:1000 SPEX	1:10 B	0.05	0.2	0.2	0.2	1	0.4
Standard 1	1:10000 SPEX	1:100 B	0.005	0.02	0.02	0.02	0.1	0.04

Table 3. Temperature (°C) recorded during sampling trips. At this range, there is no impact on water chemistry.

Site	Date								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR1	N/A	5.8	N/A	11.8	11.2	20.6	17.4	16.6	7.6
WR2	N/A	5.7	N/A	12.3	13.5	22.2	19.7	18.6	7.3
WR3	N/A	6.7	N/A	13.2	14.7	23.2	21.5	19.7	9.3
WR4	N/A	7.3	N/A	13.9	14.1	25.0	21.9	20.7	10.0
WR5	N/A	8.3	N/A	13.7	14.2	22.8	22.4	19.8	9.4
WR6	N/A	10.4	N/A	14.3	16.1	24.0	22.5	20.8	9.9
B1				12.0			18.1		
B2				12.1			19.2		
B3				12.5			19.6		
B4				13.1			21.0		

Table 4. Total Suspended Solids (mg/L).

Sample Location	Date								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR1	2.40	11.40	1.00	21.40	2.29	18.80	4.75	0.67	1.11
WR2	10.00	64.00	8.80	52.67	4.83	36.70	22.50	8.00	2.33
WR3	10.70	68.00	5.33	83.00	8.50	27.30	40.00	3.03	6.50
WR4	12.70	80.00	8.00	65.50	3.00	23.00	34.30	23.80	4.67
WR5	10.70	60.50	7.80	78.00	4.00	27.00	27.80	3.33	1.38
WR6	12.00	57.50	21.20	45.30	17.00	34.30	45.00	5.63	7.50
B1				30.25			13.50		
B2				46.70			13.00		
B3				38.67			82.00		
B4				46.70			24.00		

Table 5. pH along the White River. Overall the pH is slightly basic. The average pH at all WR sample sites is 8.02, with a standard deviation of 0.20.

Sample Location	Date									
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008	Average
WR1	7.99	7.39	8.04	7.83	8.09	7.69	8.05	7.91	7.59	7.84
WR2	8.17	7.57	8.15	7.98	8.21	7.87	8.19	8.09	8.20	8.05
WR3	8.09	7.92	8.24	7.90	8.32	7.89	8.13	8.14	8.26	8.10
WR4	8.05	7.81	8.20	7.75	8.25	7.85	8.13	7.90	8.04	8.00
WR5	8.20	7.75	8.23	7.92	8.25	7.95	8.09	8.03	8.08	8.06
WR6	8.22	7.92	8.31	7.93	8.22	7.92	8.03	8.13	8.11	8.09
B1				8.00			8.02			8.01
B2				7.95			8.17			8.06
B3				7.90			8.15			8.03
B4				7.71			7.90			7.81

Table 6. Sodium concentrations along White River.

Sample Location	Average Sodium Concentrations in mg/L								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR 1	7.20	3.30	6.43	3.28	5.83	4.11	6.97	12.06	12.95
WR 2	16.64	6.32	21.61	8.88	16.26	7.72	21.66	100.91	93.70
WR 3	8.97	6.72	8.94	5.22	7.86	5.64	7.19	17.84	18.24
WR 4	54.21	7.50	19.06	15.33	39.20	12.82	39.59	153.75	125.70
WR 5	42.88	8.47	19.08	14.42	31.12	12.60	27.55	146.30	113.63
WR 6	38.92	6.79	19.90	18.71	22.15	12.85	21.36	111.47	86.51
B1				7.44			6.85		
B2				3.92			4.79		
B3				7.22			8.37		
B4				9.25			10.55		

Table 7. Potassium concentrations along White River.

Sample Location	Average Potassium Concentrations in mg/L								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR 1	1.12	1.35	1.12	1.32	0.89	1.66	1.17	1.52	1.84
WR 2	1.68	2.05	1.87	2.54	1.36	2.08	1.77	4.98	5.62
WR 3	2.14	1.88	1.60	2.95	1.35	2.15	1.69	2.29	2.58
WR 4	3.40	2.27	2.23	2.71	1.88	2.21	2.24	4.41	3.80
WR 5	2.99	2.27	2.31	2.89	1.67	2.13	1.91	3.70	3.26
WR 6	3.28	2.62	2.09	2.49	1.67	2.37	2.07	3.72	3.36
B1				1.82			1.21		
B2				2.45			1.35		
B3				2.48			1.38		
B4				3.06			1.59		

Table 8. Calcium concentrations along White River.

Sample Location	Average Calcium Concentrations in mg/L								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR 1	70.18	37.71	62.70	49.33	63.74	52.29	70.15	89.07	88.54
WR 2	68.51	33.31	57.01	45.62	62.58	52.06	65.95	85.37	86.75
WR 3	65.26	27.86	53.12	39.62	58.38	51.06	59.01	63.83	63.70
WR 4	65.83	31.21	58.57	48.40	65.20	53.67	61.56	88.49	63.90
WR 5	69.29	34.69	63.78	45.38	68.47	56.86	64.05	91.14	72.67
WR 6	66.77	28.62	64.30	48.26	67.14	55.06	62.64	88.45	74.47
B1				53.58			71.18		
B2				45.74			66.69		
B3				53.06			72.39		
B4				40.46			69.00		

Table 9. Magnesium concentrations along White River

Sample Location	Average Magnesium Concentrations in mg/L								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR 1	26.14	13.85	24.72	18.52	24.93	18.80	25.65	32.55	31.43
WR 2	25.15	11.69	24.52	17.19	24.85	18.52	24.64	35.91	31.88
WR 3	23.63	9.16	23.04	14.42	22.73	17.87	21.36	28.29	26.98
WR 4	23.35	10.63	24.23	15.95	24.18	17.94	21.67	35.74	25.71
WR 5	23.98	11.54	24.87	16.03	24.61	19.00	21.99	34.10	26.22
WR 6	22.72	8.49	24.17	16.73	23.12	17.74	20.95	32.47	25.98
B1				19.17			25.59		
B2				16.36			23.54		
B3				17.47			23.93		
B4				11.93			22.20		

Table 10. Bicarbonate concentrations along White River. Calculated from Aquachem.

Sample Location	Average Bicarbonate Concentrations in mg/L								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR 1	243.24	135.96	253.83	151.19	248.43	195.58	280.50	417.18	401.54
WR 2	235.63	124.76	209.65	140.84	230.46	191.13	238.28	533.97	496.16
WR 3	223.46	104.04	211.28	128.49	225.18	192.21	229.85	318.27	310.05
WR 4	171.38	111.99	199.05	154.10	201.12	183.00	188.40	311.52	200.03
WR 5	193.53	123.97	217.68	144.00	219.90	194.94	206.45	301.08	207.39
WR 6	184.29	100.47	218.38	149.91	219.24	182.59	210.51	372.56	424.82

Table 11. Chloride concentrations along White River.

Sample Location	Average Chloride Concentrations in mg/L								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR 1	33.45	11.17	18.62	15.08	20.32	15.64	20.79	5.91	5.58
WR 2	49.39	16.71	55.65	34.90	46.00	24.77	55.67	45.34	39.92
WR 3	31.03	12.92	25.61	20.89	24.53	17.93	21.51	7.58	7.67
WR 4	59.02	16.51	50.05	37.02	43.61	26.86	37.82	26.80	16.90
WR 5	54.66	16.85	49.00	27.80	41.54	25.99	35.76	20.31	15.12
WR 6	60.14	15.59	48.67	36.40	43.89	28.56	36.63	21.95	14.25

B1				27.10			19.67		
B2				17.89			15.78		
B3				25.66			25.35		
B4				31.31			32.03		

Table 12. Sulfate concentrations along White River.

Sample Location	Average Sulfate Concentrations in mg/L								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR 1	32.72	14.06	30.72	17.08	29.47	19.65	32.93	32.49	41.83
WR 2	38.72	12.98	37.17	18.11	34.15	20.86	34.99	78.66	81.34
WR 3	44.31	14.44	36.46	19.39	33.56	23.05	28.01	43.70	45.87
WR 4	139.95	19.31	50.90	32.13	113.55	40.31	112.32	390.03	334.03
WR 5	117.67	23.49	53.05	40.95	94.61	42.52	83.39	392.92	329.22
WR 6	97.64	14.95	53.47	47.77	64.10	38.72	58.31	251.43	107.13
B1				23.33			40.02		
B2				18.12			28.90		
B3				27.95			44.85		
B4				25.67			42.87		

Table 13. Nitrate concentrations along White River.

Sample Location	Average Nitrate Concentrations in mg/L								
	12/7/2007	3/21/2008	4/25/2008	5/9/2008	5/21/2008	6/9/2008	7/2/2008	9/8/2008	10/27/2008
WR 1	23.77	22.51	9.08	55.99	15.50	19.99	4.61	0.34	0.35
WR 2	12.05	10.27	4.40	29.31	7.67	15.22	6.32	3.94	13.62
WR 3	11.45	7.08	1.98	22.75	4.89	11.35	6.28	0.47	0.30
WR 4	16.29	7.01	4.21	13.98	6.50	10.70	8.69	10.55	9.61
WR 5	12.87	6.85	3.95	17.83	5.68	11.75	7.66	7.40	7.81
WR 6	14.10	5.66	3.14	11.41	5.76	13.80	8.29	4.14	6.63
B1				15.94			4.58		
B2				22.99			5.60		
B3				18.92			5.16		
B4				37.88			4.97		

Table 14a. Trace metals concentrations (ppb) for 5/9/2008 White River sites.

		WR1 5-9 Sed	**WR2 5-9 Sed**	**WR3 5-9 Sed**	**WR4 5-9 Sed**	**WR5 5-9 Sed**	**WR6 5-9 Sed**
Analyte	Mass	**Conc. Mean**	**Conc. Mean**	**Conc. Mean**	**Conc. Mean**	**Conc. Mean**	**Conc. Mean**

Al	27	507245.317	768844.223	744854.046	676828.013	229970.537	757109.478
V	51	2971.574	3819.757	3717.319	2698.302	1061.287	4417.014
Cr	52	800.843	1235.091	1035.248	2367.405	1147.519	7370.644
Mn	55	139461.214	247428.611	350282.691	230053.034	84278.193	354200.984
Fe	56	1.83038E+12	1.91299E+12	1.90725E+12	1.81816E+12	1.05257E+12	2.27054E+12
Co	59	1772.03	2559.61	2556.916	1928.789	1026.485	2617.008
Ni	60	1803.414	3229.337	2925.185	3606.788	971.51	6020.316
Cu	63	4058.033	11257.012	7545.404	16643.003	2996.57	20356.94
Cu	65	4105.035	10451.45	7005.919	16919.757	3019.088	20753.271
Zn	66	4655.539	13930.458	7551.791	32132.471	9040.161	41974.29
As	75	1926.531	2001.395	2087.847	1414.378	800.36	2739.125
Sr	86	66.102	69.715	112.662	67.344	65.833	118.336
Sr	87	77.998	80.555	122.123	77.493	69.266	129.279
Mo	96	156.965	-56.653	-34.486	178.48	142.885	23.378
Mo	98	332.419	220.934	226.419	356.262	96.772	295.625
Cd	114	3.752	3.261	4.049	8.509	2.871	12.613
Sn	120	66.199	410.087	112.332	1035.176	176.971	602.926
La	139	33.066	35.942	43.074	21.552	14.953	44.18
Nd	142	37.176	41.531	48.346	21.407	15.852	49.889
Nd	144	37.377	41.426	50.008	21.83	15.704	49.588
Sm	149	10.087	11.624	13.555	5.806	3.968	12.8
Eu	151	3.523	3.803	4.59	2.355	1.353	4.242
Sm	152	11.844	12.822	15.266	7.758	4.826	14.869
Eu	153	4.133	4.275	5.149	2.865	1.701	4.973
Gd	156	26.441	27.507	33.999	19.192	10.728	30.177
Gd	158	18.165	19.537	22.604	10.792	6.926	20.964
Lu	175	3.645	3.682	4.126	2.76	1.233	3.719
Hg	200	3.235	3.278	2.392	5.109	1.241	5.477
Hg	202	2.868	3.177	2.873	4.329	1.098	4.69

Pb	204	106.79	102.54	92.082	897.887	294.815	451.005
Pb	206	114.956	115.433	102.75	976.578	318.598	488.534
Pb	208	110.07	110.825	97.959	946.584	308.421	473.349
Rh	103						
Cr	53	706.249	1180.111	897.833	2223.183	910.659	6598.11
Ni	62	1885.865	3360.693	3048.191	3711.712	997.981	6223.817
Zn	67	4407.718	12272.289	6963.105	24583.059	7808.226	32325.723
Zn	68	4496.956	13015	7157.084	30066.363	8376.488	39386.881
Ag	107	18.268	30.648	26.88	19.76	5.824	32.468
Ag	109	1.077	2.251	1.83	2.616	0.869	4.069
Cd	111	7.299	8.413	7.728	14.194	4.551	18.427

Table 14b. Trace metals concentrations (ppb) for 5/9/2008 Background sites.

		B1 5-9 Sed	**B2 5-9 Sed**	**B3 5-9 Sed**	**B4 5-9 Sed**
Analyte	Mass	**Conc. Mean (ppb)**	**Conc. Mean**	**Conc. Mean**	**Conc. Mean**
Al	27	172564.323	684288.997	150306.279	1169118.223
V	51	1265.317	4068.378	1012.292	5952.519
Cr	52	473.752	1062.68	616.927	1274.488
Mn	55	61132.951	311077.782	87412.688	374540.507
Fe	56	700064.279	1.89966E+12	1194552.173	2.00975E+12
Co	59	1130.849	3081.871	933.926	3957.744
Ni	60	1098.615	3355.506	899.594	4283.043
Cu	63	1888.751	6358.554	1991.868	8300.739
Cu	65	1901.812	6106.345	2017.777	7659.541
Zn	66	1729.775	7020.534	5932.887	28666.618
As	75	734.455	2715.658	801.636	3588.286
Sr	86	81.602	110.655	48.121	104.65

Sr	87	86.179	136.105	48.925	112.069
Mo	96	256.018	276.48	171.095	81.423
Mo	98	213.895	526.646	127.435	399.952
Cd	114	2.516	4.671	3.079	10.363
Sn	120	87.104	72.393	204.941	101.165
La	139	14.102	34.205	11.174	102.833
Nd	142	15.421	36.268	11.389	106.286
Nd	144	15.457	36.654	11.093	106.388
Sm	149	5.051	9.991	2.685	28.976
Eu	151	2.407	3.64	1.087	10.699
Sm	152	5.661	12.14	3.532	36.027
Eu	153	2.706	4.46	1.326	12.758
Gd	156	13.526	29.28	7.998	78.081
Gd	158	7.839	17.568	5.007	48.09
Lu	175	2.703	3.875	1.122	8.128
Hg	200	11.174	7.472	3.782	3.831
Hg	202	11.073	6.19	3.588	3.697
Pb	204	75.164	115.291	228.936	280.99
Pb	206	82.167	126.214	247.733	307.908
Pb	208	78.846	121.242	241.679	296.108
Rh	103				
Cr	53	300.944	929.329	478.555	1527.573
Ni	62	1151.347	3529.027	930.869	4525.402
Zn	67	1657.045	6543.851	5125.737	22525.69
Zn	68	1650.858	6660.903	5467.601	23727.804
Ag	107	11.57	28.545	5.762	36.945
Ag	109	3.238	2.098	0.176	3.3
Cd	111	4.355	9.605	4.342	16.097

Table 15. Cadmium concentrations in sediment for 5/9/2008.

Sample Location	Concentration	
	ppb	mg/kg
WR 1	5.53	5.53E-03
WR 2	5.84	5.84E-03
WR 3	5.89	5.89E-03
WR 4	11.35	1.14E-02
WR 5	3.71	3.71E-03
WR 6	15.52	1.55E-02
B1	3.44	3.44E-03
B2	7.14	7.14E-03
B3	3.71	3.71E-03
B4	13.23	1.32E-02

Table 16. Chromium concentrations in sediment for 5/9/2008.

Sample Location	Concentration	
	ppb	mg/kg
WR 1	753.55	0.75
WR 2	1207.6	1.21
WR 3	966.54	0.97
WR 4	2295.3	2.30
WR 5	1029.1	1.03
WR 6	6984.4	6.98
B1	387.35	0.39
B2	996	1.00
B3	547.74	0.55
B4	1401	1.40

Table 17. Copper concentrations in sediment for 5/9/2008.

Sample Location	Concentration	
	ppb	mg/kg
WR 1	4081.53	4.08
WR 2	10854.2	10.85
WR 3	7275.66	7.28
WR 4	16781.4	16.78
WR 5	3007.83	3.01
WR 6	20555.1	20.56
B1	1895.28	1.90
B2	6232.45	6.23
B3	2004.82	2.00
B4	7980.14	7.98

Table 18. Nickel concentrations in sediment for 5/9/2008.

Sample Location	Concentration	
	ppb	mg/kg
WR 1	1844.64	1.84
WR 2	3295.02	3.30
WR 3	2986.69	2.99
WR 4	3659.25	3.66
WR 5	984.746	0.98
WR 6	6122.07	6.12
B1	1124.98	1.12
B2	3442.27	3.44
B3	915.23	0.92
B4	4404.22	4.40

Table 19. Tin concentrations in sediment for 5/9/2008.

Sample Location	Concentration	
	ppb	mg/kg
WR 1	66.199	0.07
WR 2	410.087	0.41
WR 3	112.332	0.11
WR 4	1035.176	1.04
WR 5	176.971	0.18
WR 6	602.926	0.60
B1	87.10	0.09
B2	72.39	0.07
B3	204.94	0.20
B4	101.17	0.10

Table 20. Zinc concentrations in sediment for 5/9/2008.

Sample Location	Concentration	
	ppb	mg/kg
WR 1	4520.07	4.52
WR 2	13072.6	13.07
WR 3	7223.99	7.22
WR 4	28927.3	28.93
WR 5	8408.29	8.41
WR 6	37895.6	37.90
B1	1679.23	1.68
B2	6741.76	6.74
B3	5508.74	5.51
B4	24973.37	24.97

Table 21. Water type calculations from Aquachem®

Station ID	Sampling Date	Water Type
WR 1	12/7/2007	Ca-Mg-HCO3
WR 1	3/21/2008	Ca-Mg-HCO3
WR 1	4/25/2008	Ca-Mg-HCO3
WR 1	5/9/2008	Ca-Mg-HCO3-NO3
WR 1	5/21/2008	Ca-Mg-HCO3
WR 1	6/9/2008	Ca-Mg-HCO3
WR 1	7/2/2008	Ca-Mg-HCO3
WR 1	9/8/2008	Ca-Mg-HCO3
WR 1	10/27/2008	Ca-Mg-HCO3
WR 2	12/7/2007	Ca-Mg-HCO3-Cl
WR 2	3/21/2008	Ca-Mg-HCO3
WR 2	4/25/2008	Ca-Mg-HCO3-Cl
WR 2	5/9/2008	Ca-Mg-HCO3-Cl
WR 2	5/21/2008	Ca-Mg-HCO3-Cl
WR 2	6/9/2008	Ca-Mg-HCO3
WR 2	7/8/2008	Ca-Mg-HCO3-Cl
WR 2	9/8/2008	Na-Ca-Mg-HCO3

WR 2	10/27/2008	Ca-Na-Mg-HCO3
WR 3	12/7/2007	Ca-Mg-HCO3
WR 3	3/21/2008	Ca-Mg-HCO3
WR 3	4/25/2008	Ca-Mg-HCO3
WR 3	5/9/2008	Ca-Mg-HCO3
WR 3	5/21/2008	Ca-Mg-HCO3
WR 3	6/9/2008	Ca-Mg-HCO3
WR 3	7/2/2008	Ca-Mg-HCO3
WR 3	9/8/2008	Ca-Mg-HCO3
WR 3	10/27/2008	Ca-Mg-HCO3
WR 4	12/7/2007	Ca-Na-Mg-SO4-HCO3-Cl
WR 4	3/21/2008	Ca-Mg-HCO3
WR 4	4/25/2008	Ca-Mg-HCO3-Cl
WR 4	5/9/2008	Ca-Mg-HCO3-Cl
WR 4	5/21/2008	Ca-Mg-Na-HCO3-SO4
WR 4	6/9/2008	Ca-Mg-HCO3
WR 4	7/2/2008	Ca-Mg-Na-HCO3-SO4
WR 4	9/8/2008	Na-Ca-Mg-SO4-HCO3
WR 4	10/27/2008	Na-Ca-SO4-HCO3
WR 5	12/7/2007	Ca-Mg-Na-HCO3-SO4-Cl
WR 5	3/21/2008	Ca-Mg-HCO3
WR 5	4/25/2008	Ca-Mg-HCO3-Cl
WR 5	5/9/2008	Ca-Mg-HCO3
WR 5	5/21/2008	Ca-Mg-HCO3-SO4
WR 5	6/9/2008	Ca-Mg-HCO3
WR 5	7/2/2008	Ca-Mg-HCO3-SO4
WR 5	9/8/2008	Na-Ca-Mg-SO4-HCO3
WR 5	10/27/2008	Na-Ca-SO4-HCO3
WR 6	12/7/2007	Ca-Mg-Na-HCO3-SO4-Cl
WR 6	3/21/2008	Ca-Mg-HCO3

WR 6	4/25/2008	Ca-Mg-HCO3-Cl
WR 6	5/9/2008	Ca-Mg-HCO3-Cl-SO4
WR 6	5/21/2008	Ca-Mg-HCO3-SO4
WR 6	6/9/2008	Ca-Mg-HCO3
WR 6	7/2/2008	Ca-Mg-HCO3-SO4
WR 6	9/8/2008	Na-Ca-Mg-HCO3-SO4
WR 6	10/27/2008	Na-Ca-Mg-HCO3-SO4

Table 22. Saturation indices with relation to calcite.

Station ID	Sampling Date	SI (Calcite)
WR 1	12/7/2007	0.6533
WR 1	3/21/2008	-0.613
WR 1	4/25/2008	0.6824
WR 1	5/9/2008	0.0498
WR 1	5/21/2008	0.6016
WR 1	6/9/2008	0.1809
WR 1	7/2/2008	0.7397
WR 1	9/8/2008	0.8403
WR 1	10/27/2008	0.3753
WR 2	12/7/2007	0.8008
WR 2	3/21/2008	-0.5149
WR 2	4/25/2008	0.6636
WR 2	5/9/2008	0.1499
WR 2	5/21/2008	0.7077
WR 2	6/9/2008	0.3672

WR 2	7/8/2008	0.807
WR 2	9/8/2008	1.0805
WR 2	10/27/2008	1.0055
WR 3	12/7/2007	0.6873
WR 3	3/21/2008	-0.2958
WR 3	4/25/2008	0.733
WR 3	5/9/2008	-0.002
WR 3	5/21/2008	0.7995
WR 3	6/9/2008	0.3974
WR 3	7/2/2008	0.7296
WR 3	9/8/2008	0.8628
WR 3	10/27/2008	0.8193
WR 4	12/7/2007	0.4933
WR 4	3/21/2008	-0.3239
WR 4	4/25/2008	0.6965
WR 4	5/9/2008	0.0074
WR 4	5/21/2008	0.6807
WR 4	6/9/2008	0.3716
WR 4	7/2/2008	0.6258
WR 4	9/8/2008	0.6358
WR 4	10/27/2008	0.3232
WR 5	12/7/2007	0.7184
WR 5	3/21/2008	-0.2859
WR 5	4/25/2008	0.7936
WR 5	5/9/2008	0.1129
WR 5	5/21/2008	0.7471
WR 5	6/9/2008	0.4854
WR 5	7/2/2008	0.662
WR 5	9/8/2008	0.7487
WR 5	10/27/2008	0.4256

WR 6	12/7/2007	0.7106
WR 6	3/21/2008	-0.2403
WR 6	4/25/2008	0.8734
WR 6	5/9/2008	0.1694
WR 6	5/21/2008	0.7507
WR 6	6/9/2008	0.4349
WR 6	7/2/2008	0.6173
WR 6	9/8/2008	0.9733
WR 6	10/27/2008	0.836

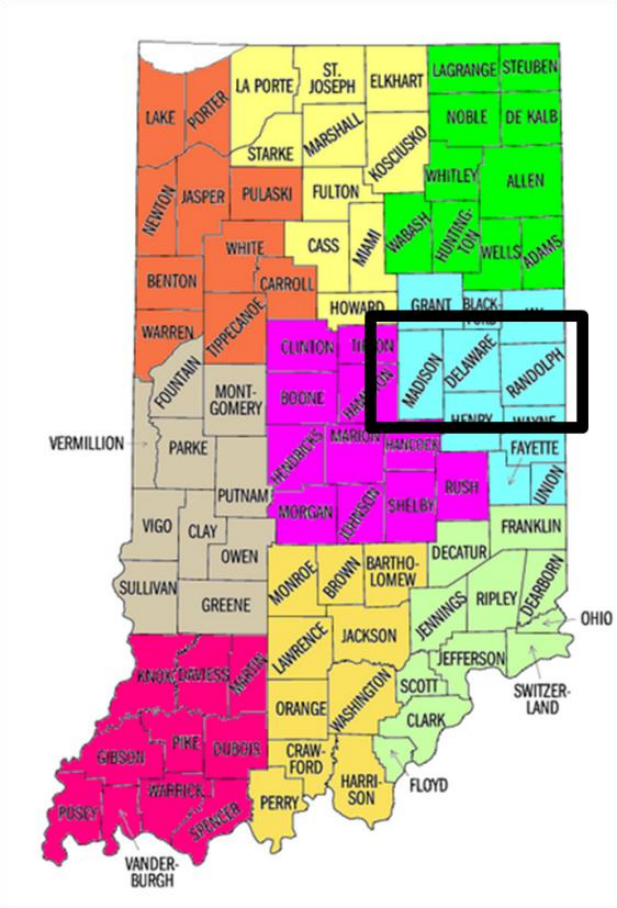

Fig. 1. Location of study area in east-central Indiana.

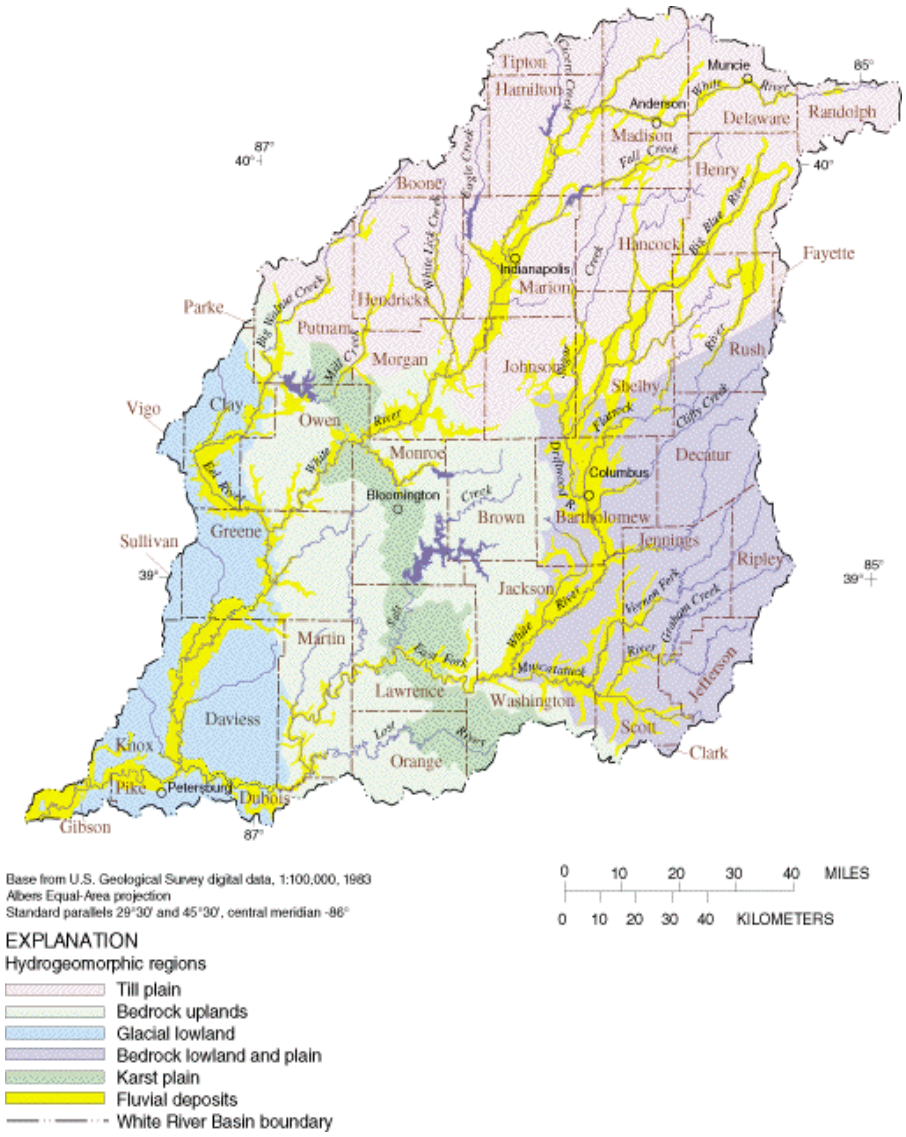

Fig. 2. Hydrogeomorphic map of White River watershed (USGS 2001).

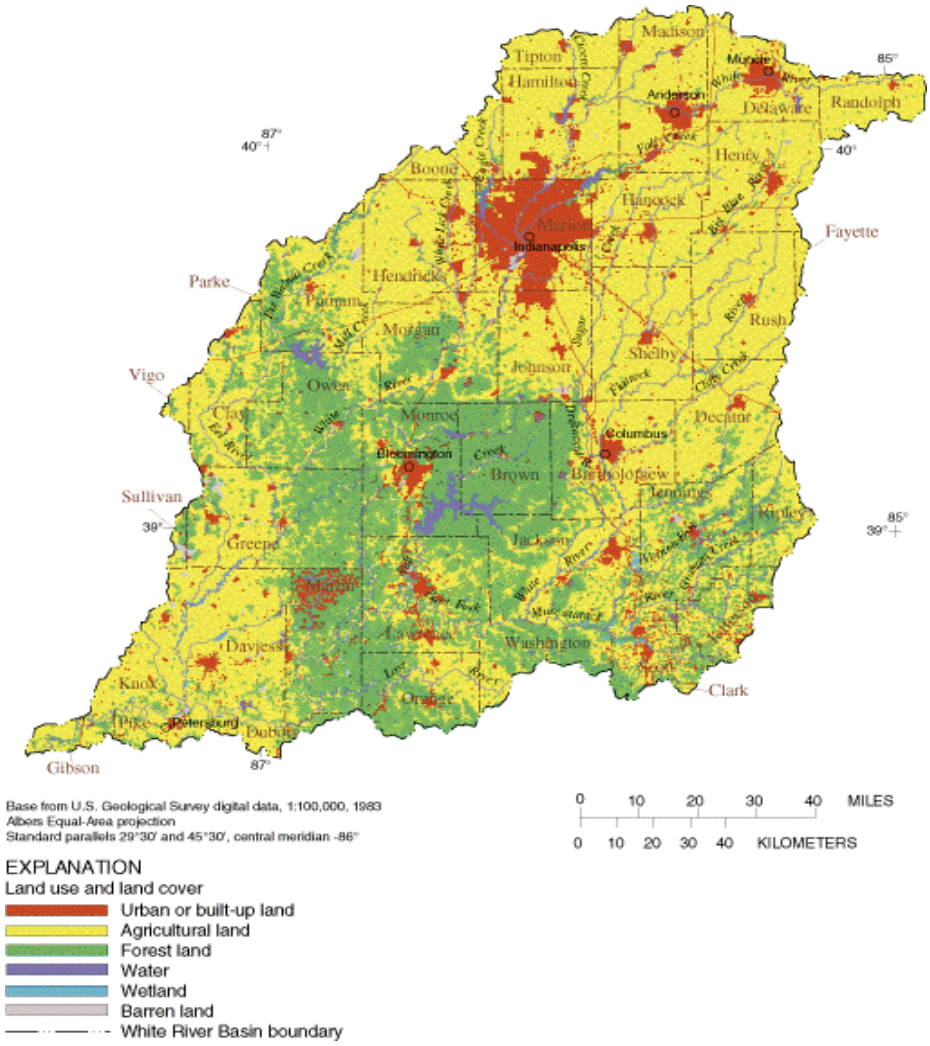

Fig. 3. Land Use Map of White River watershed (USGS 2001).

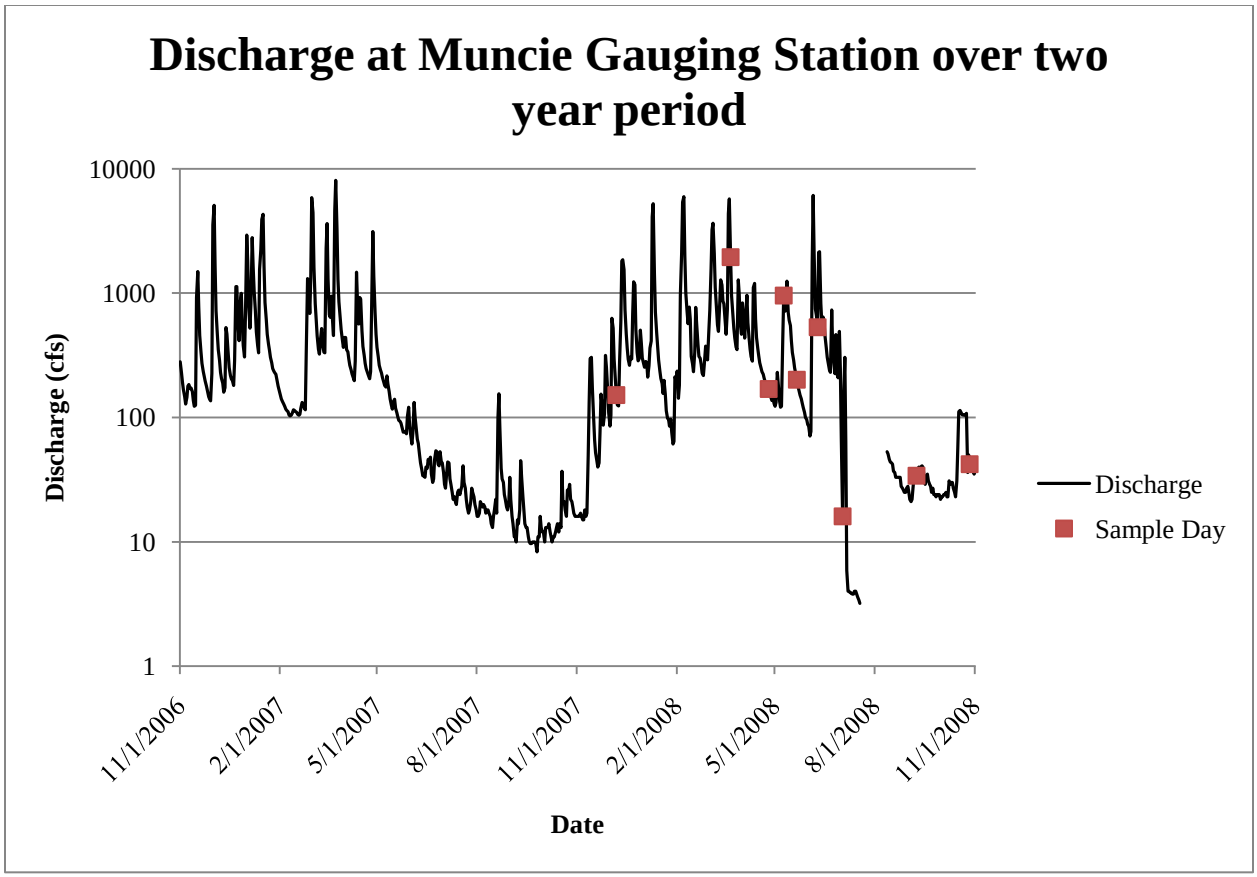

Fig. 4. Hydrograph over a two year period. Gauging Station 03347000. Red squares indicate days that samples were taken.

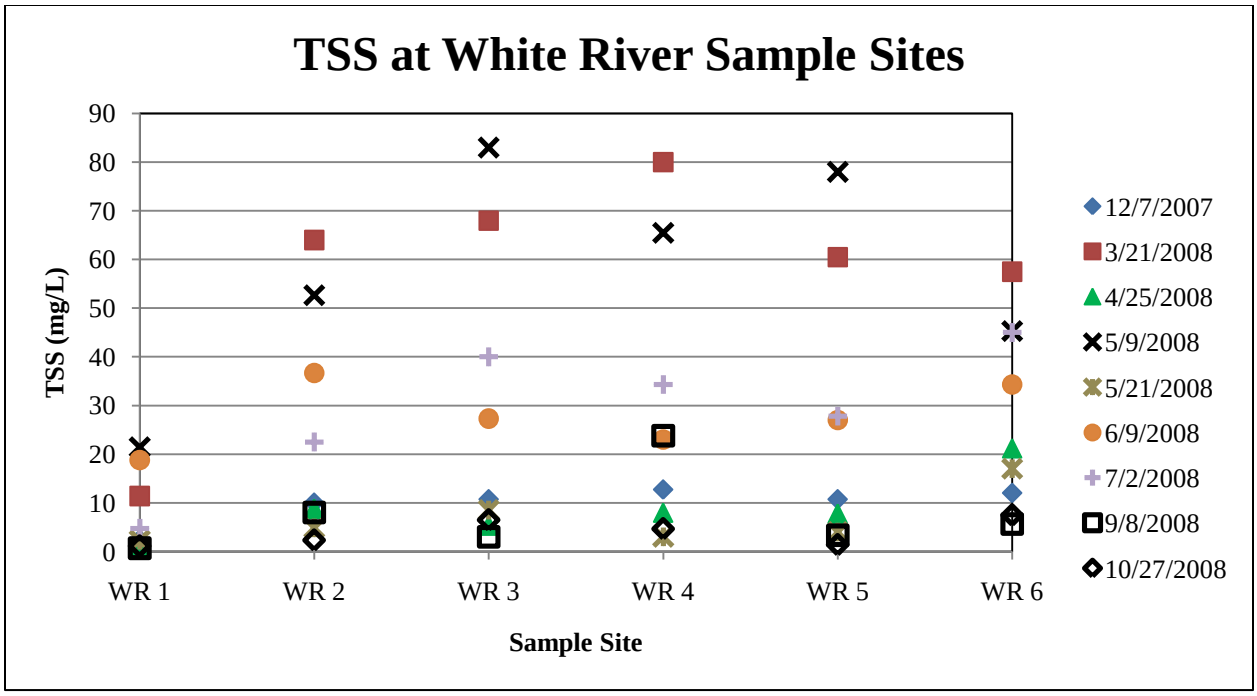

Fig. 5. Total Suspended Solids for all sample dates.

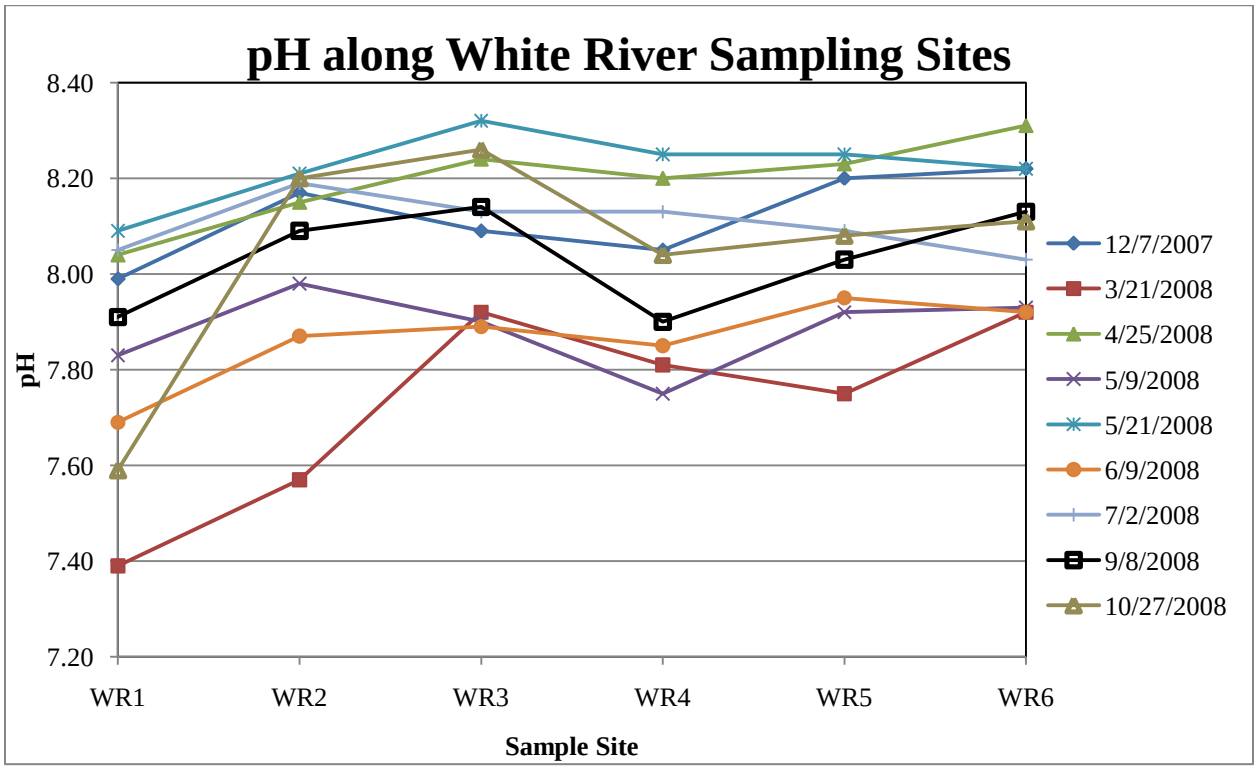

Fig. 6. pH along White River Sampling Sites.

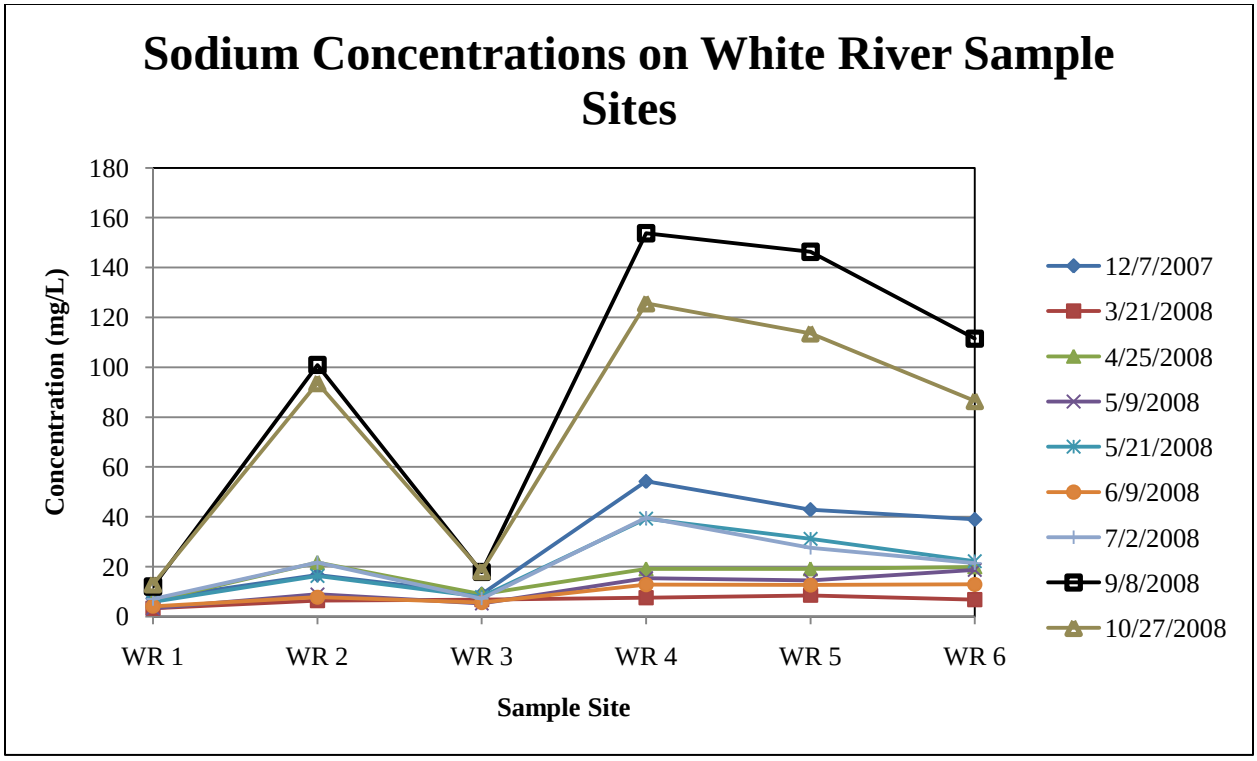

Fig. 7. Sodium concentrations along White River Sample Sites.

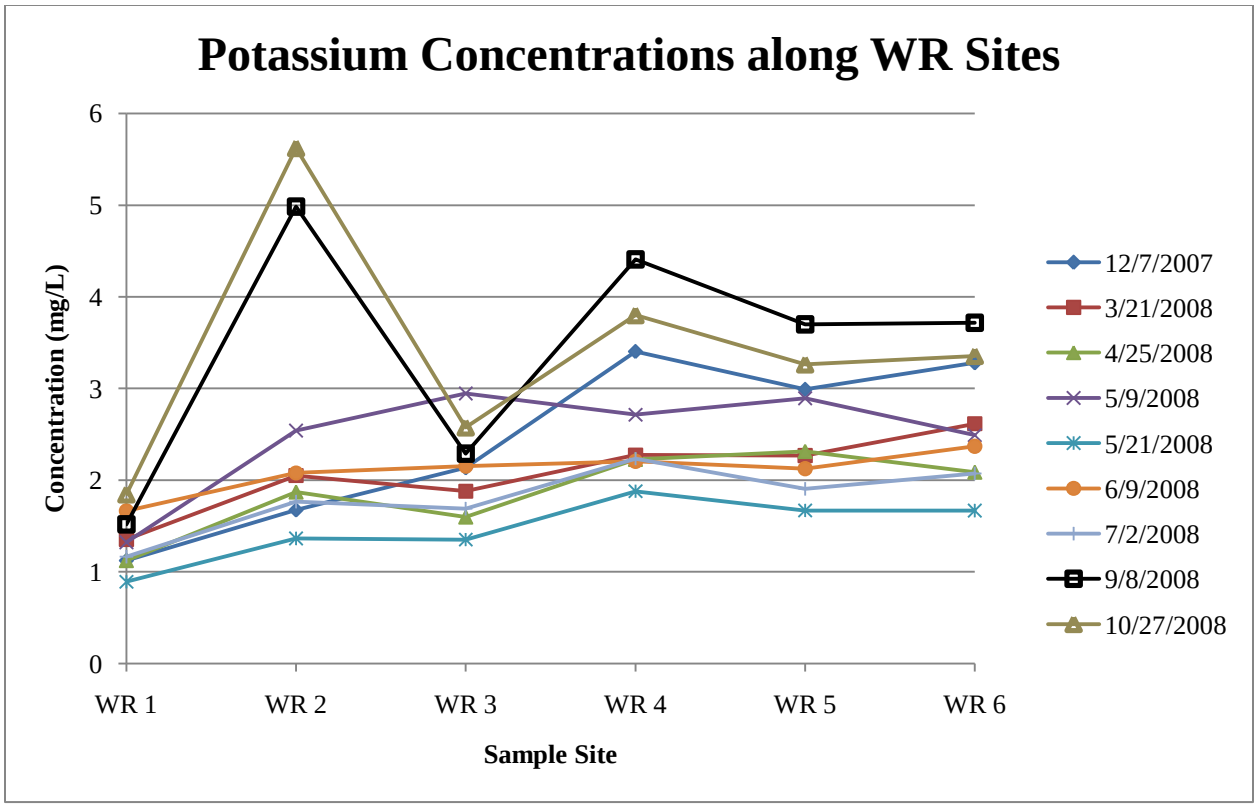

Fig. 8. Potassium concentrations along White River sample sites.

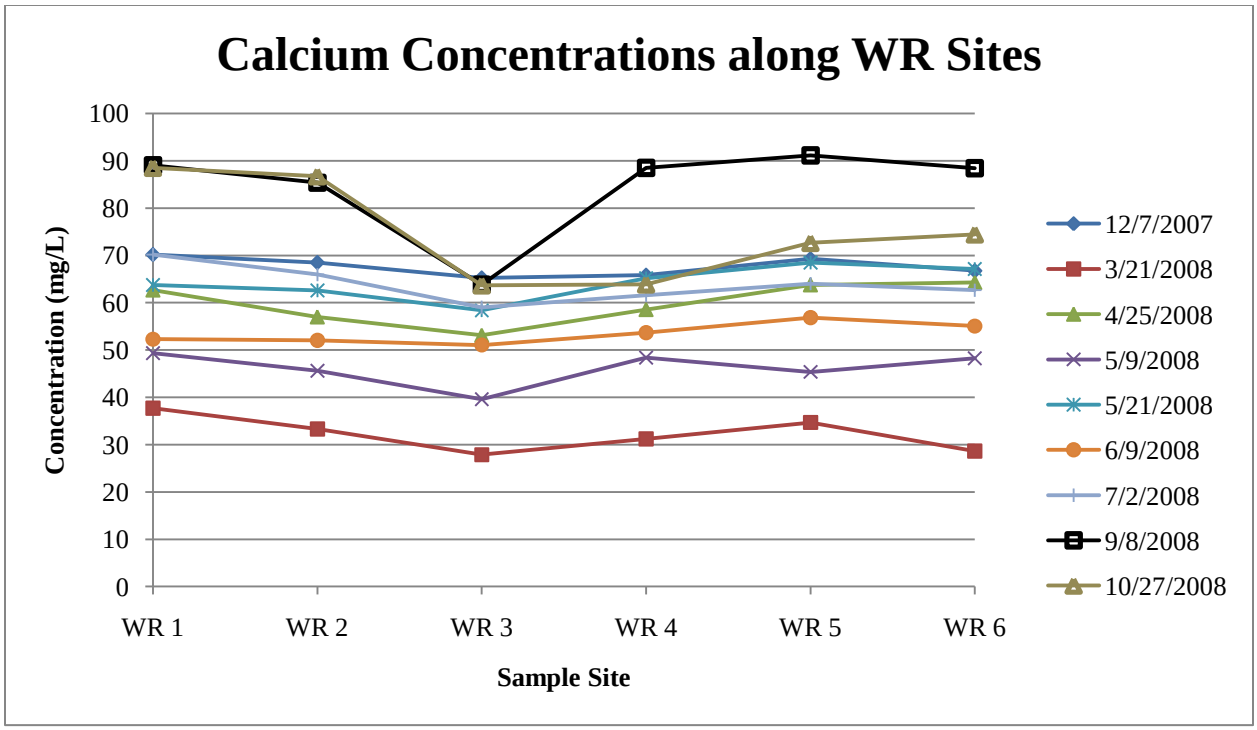

Fig. 9. Calcium concentrations along White River sample sites.

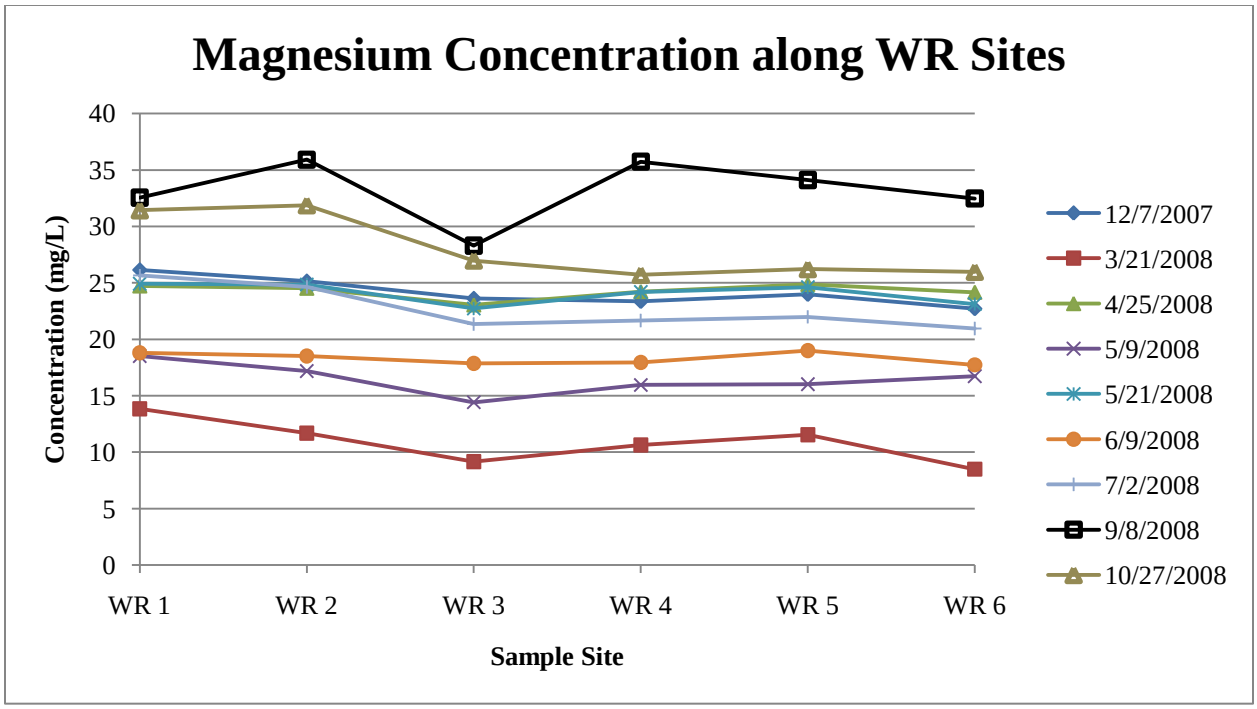

Fig. 10. Magnesium concentrations along White River sample sites.

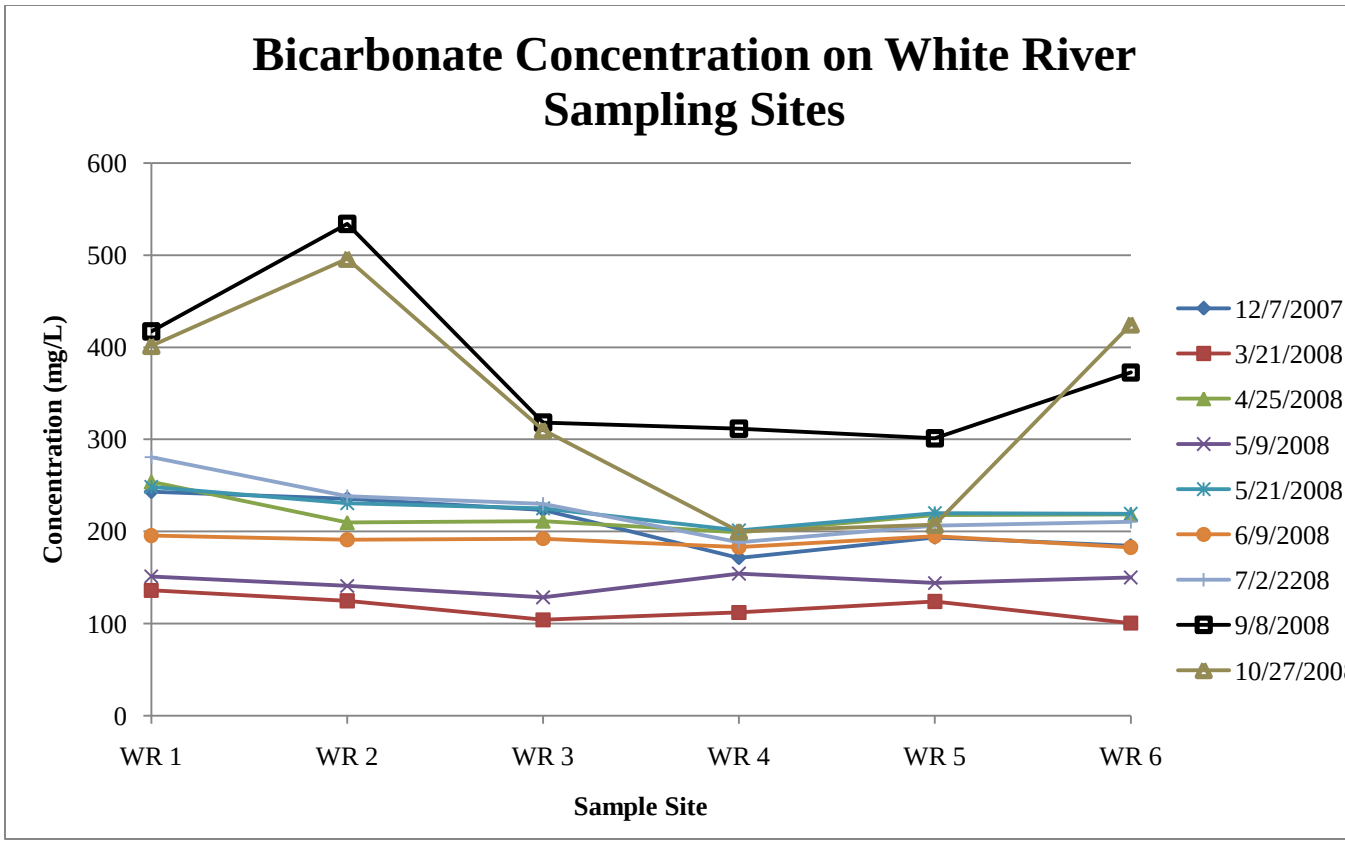

Fig. 11. Bicarbonate concentration along White River sample sites.

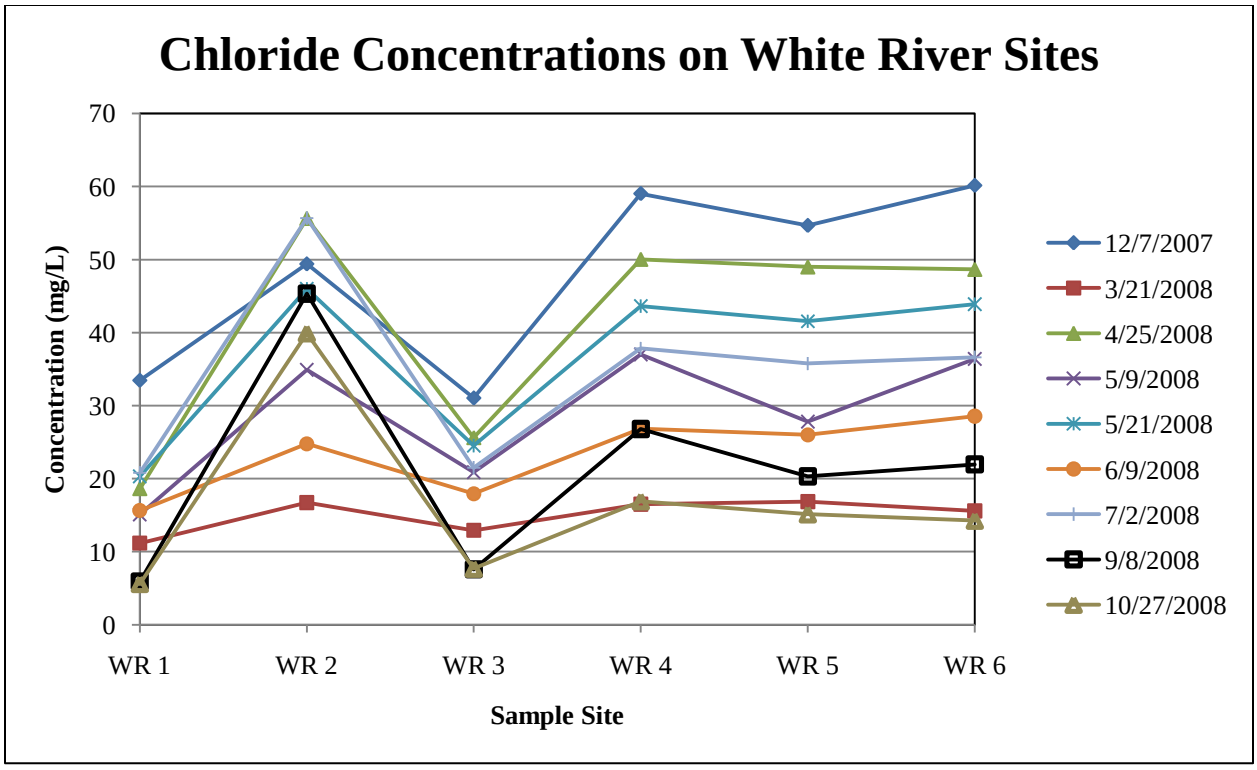

Fig. 12. Chloride concentrations along White River sample sites.

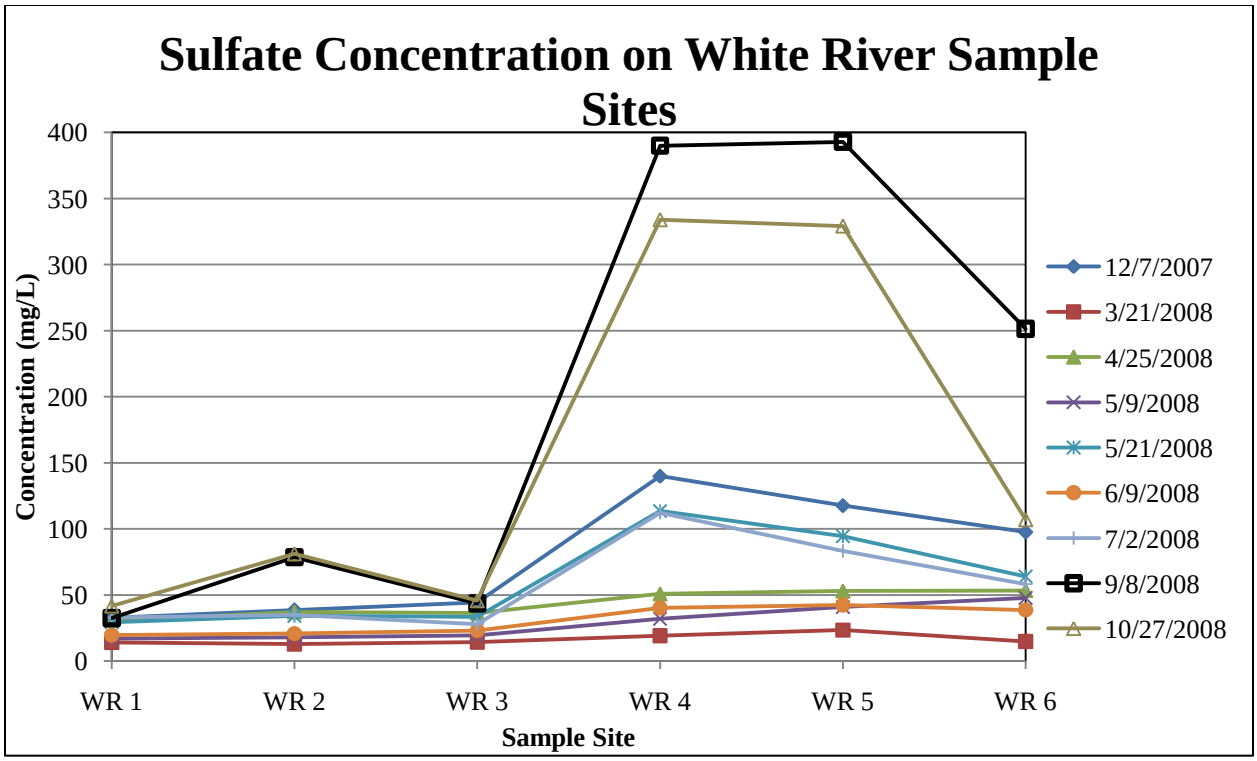

Fig. 13. Sulfate concentrations along White River sample sites.

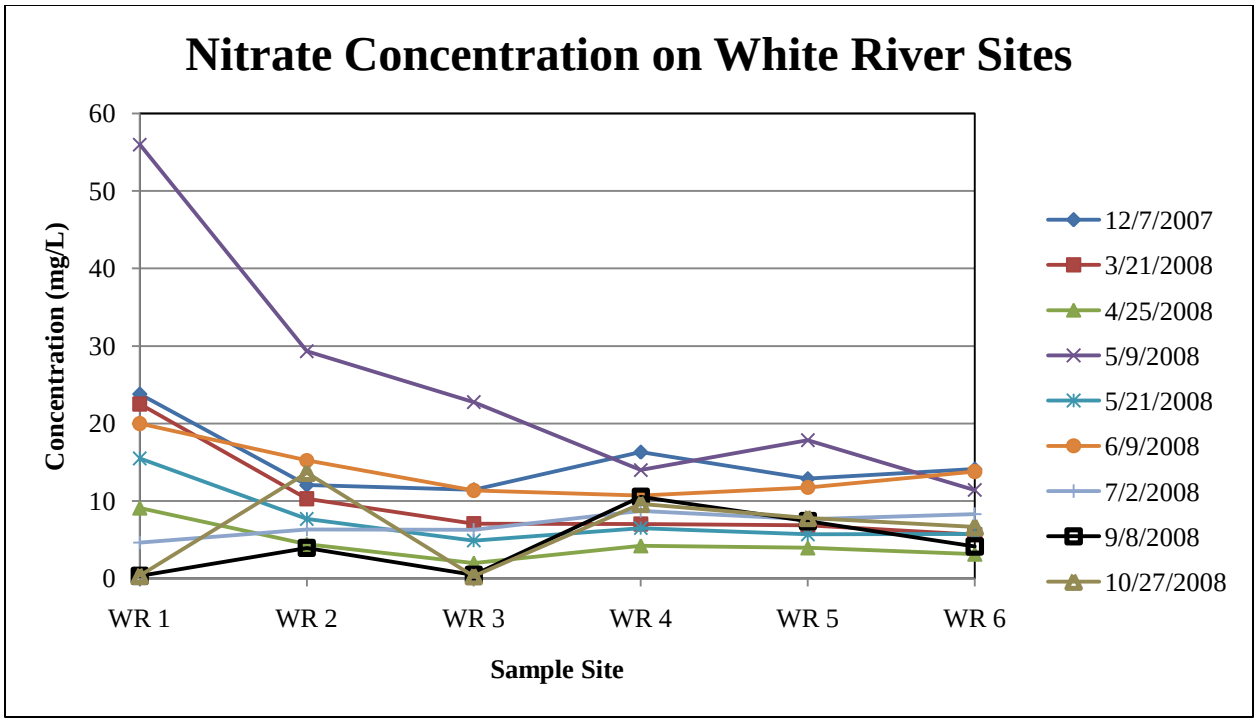

Fig. 14. Nitrate concentrations are generally higher in the agricultural background setting.

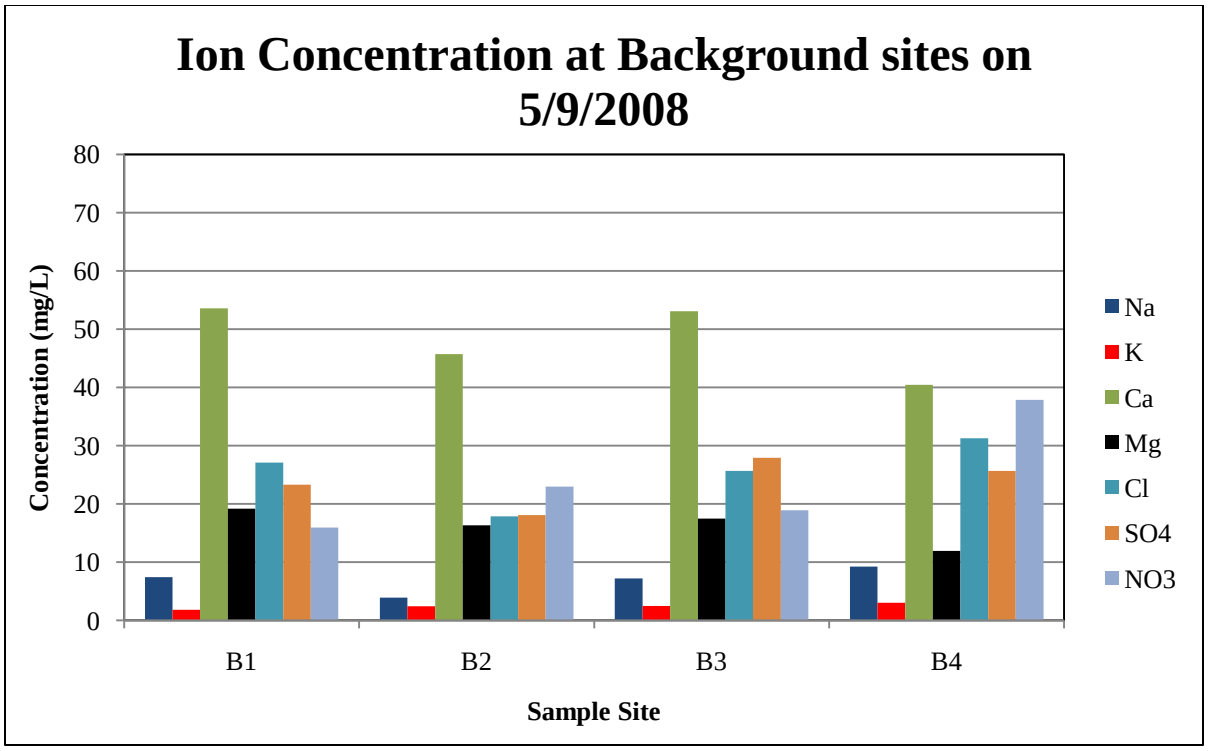

Fig. 15a. Background concentrations at the four background sites. Substantial amounts of nitrate in the water during spring planting period.

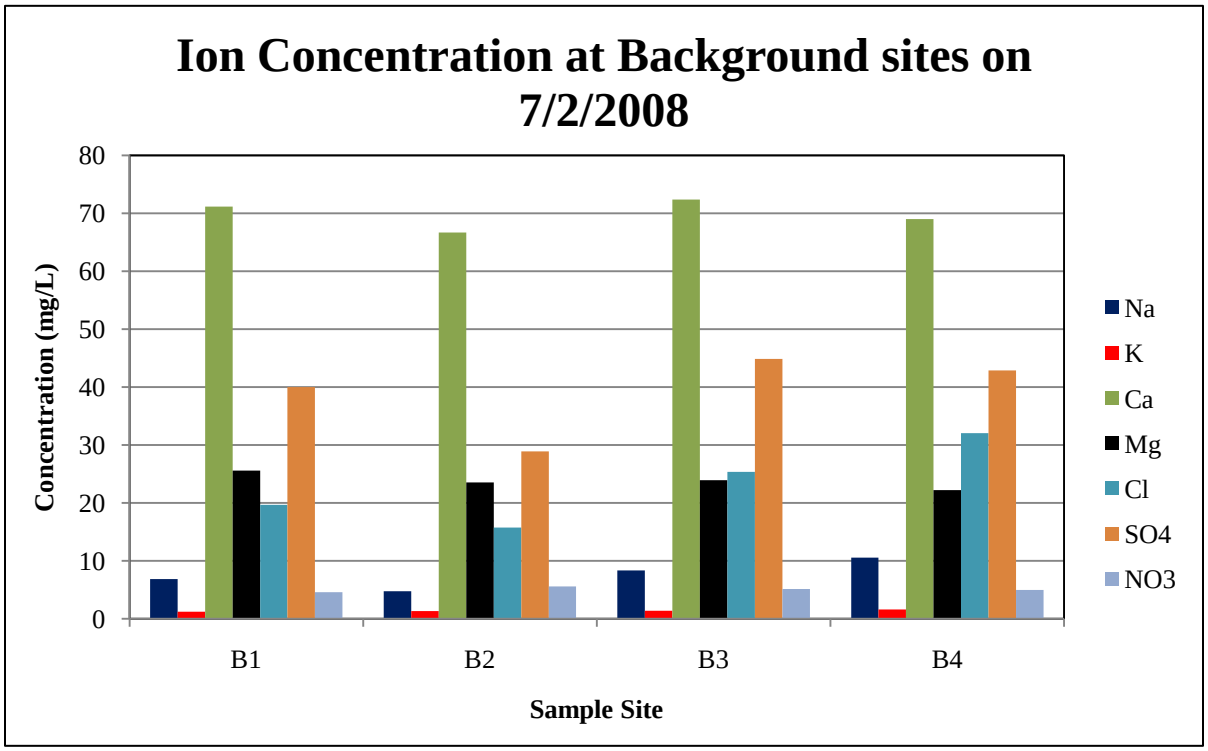

Fig. 15b. Low flow sample date.

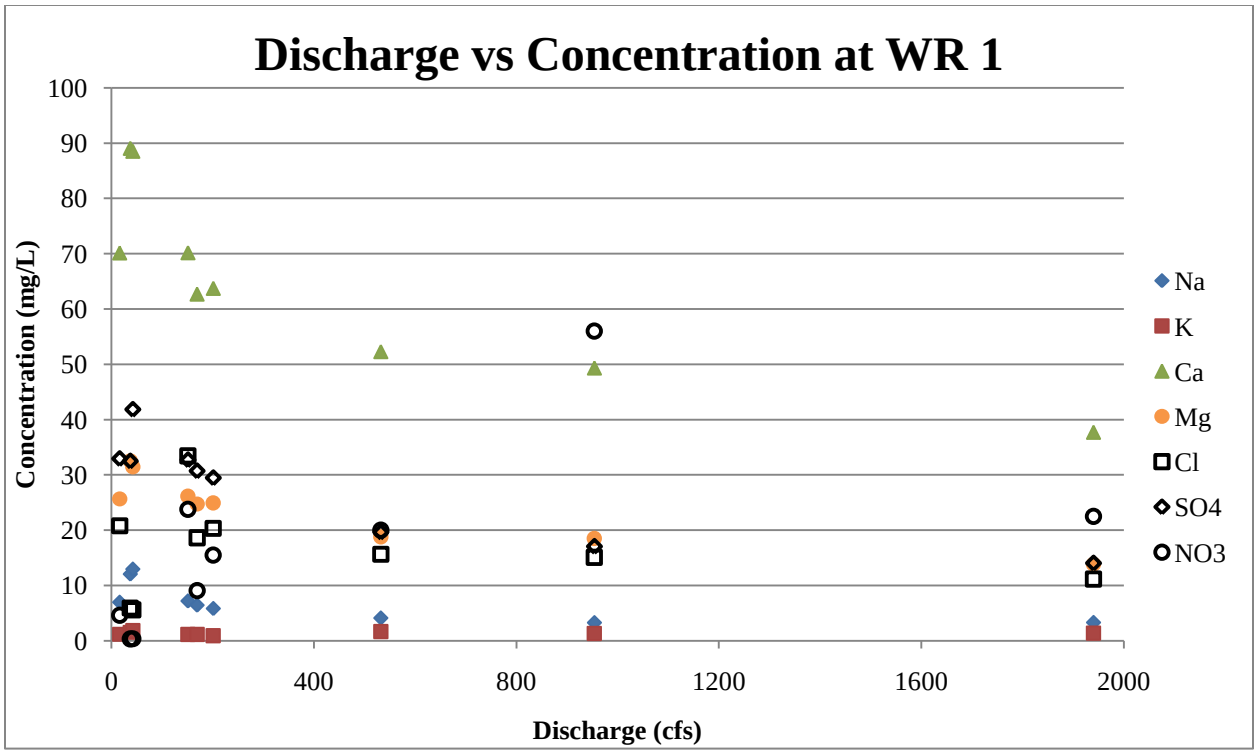

Fig. 16a. Discharge vs. Concentration at WR 1.

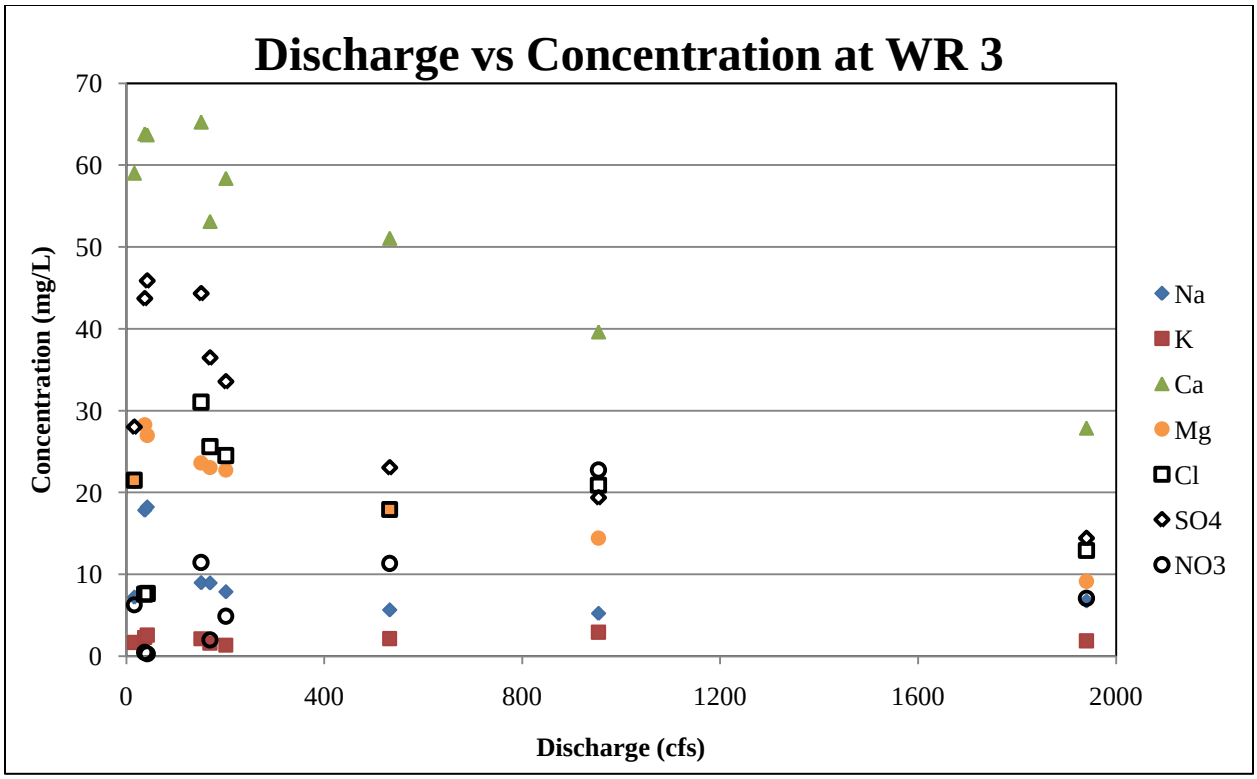

Fig. 16b. Discharge vs. Concentration at WR 3.

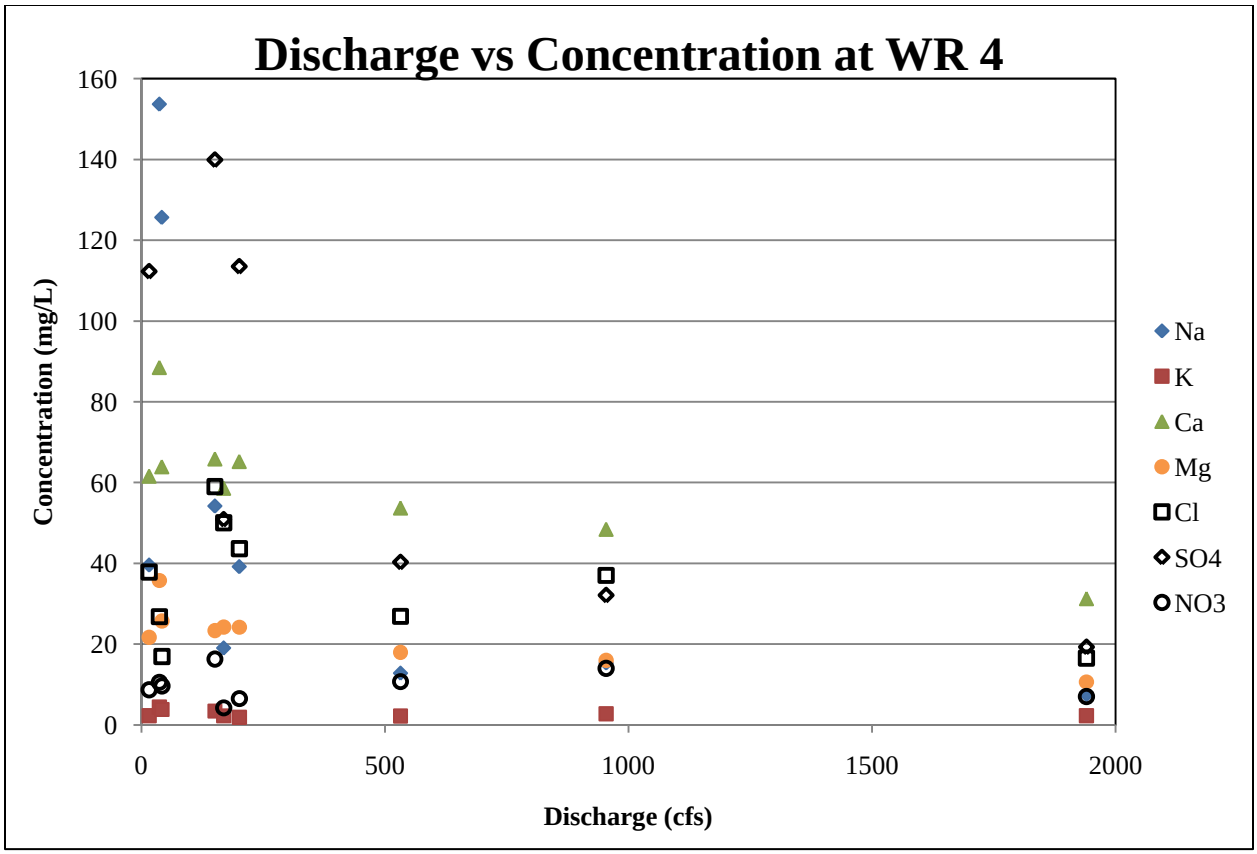

Fig. 16c. Discharge vs. Concentration at WR 4.

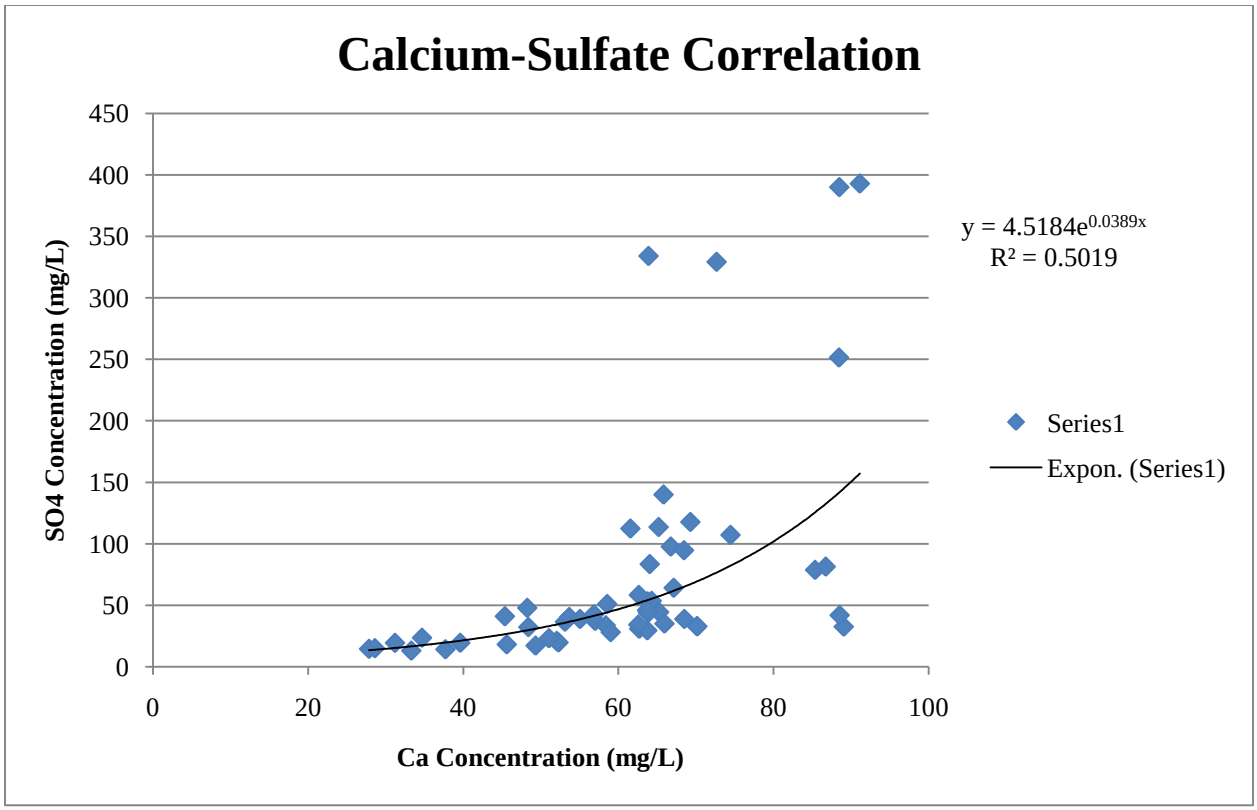

Fig. 17. Calcium-sulfate correlation graph.

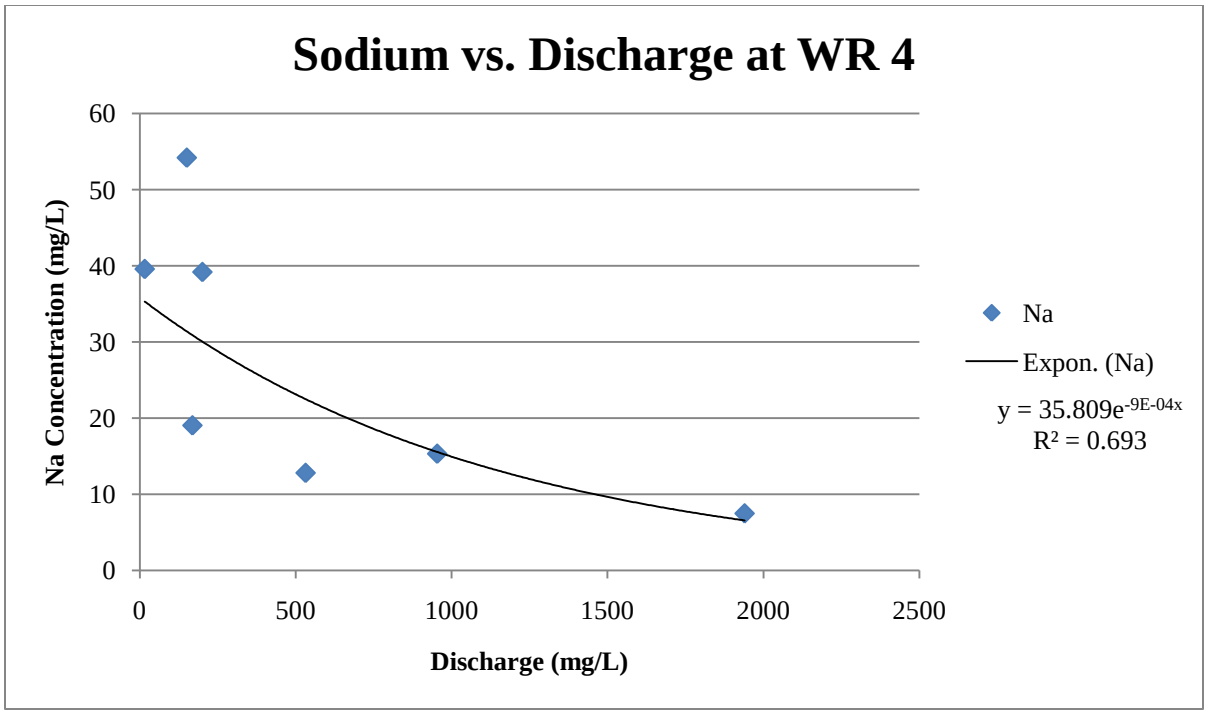

Fig. 18a. Sodium vs. discharge at WR 4. This excludes last two sample runs and shows an exponential relationship.

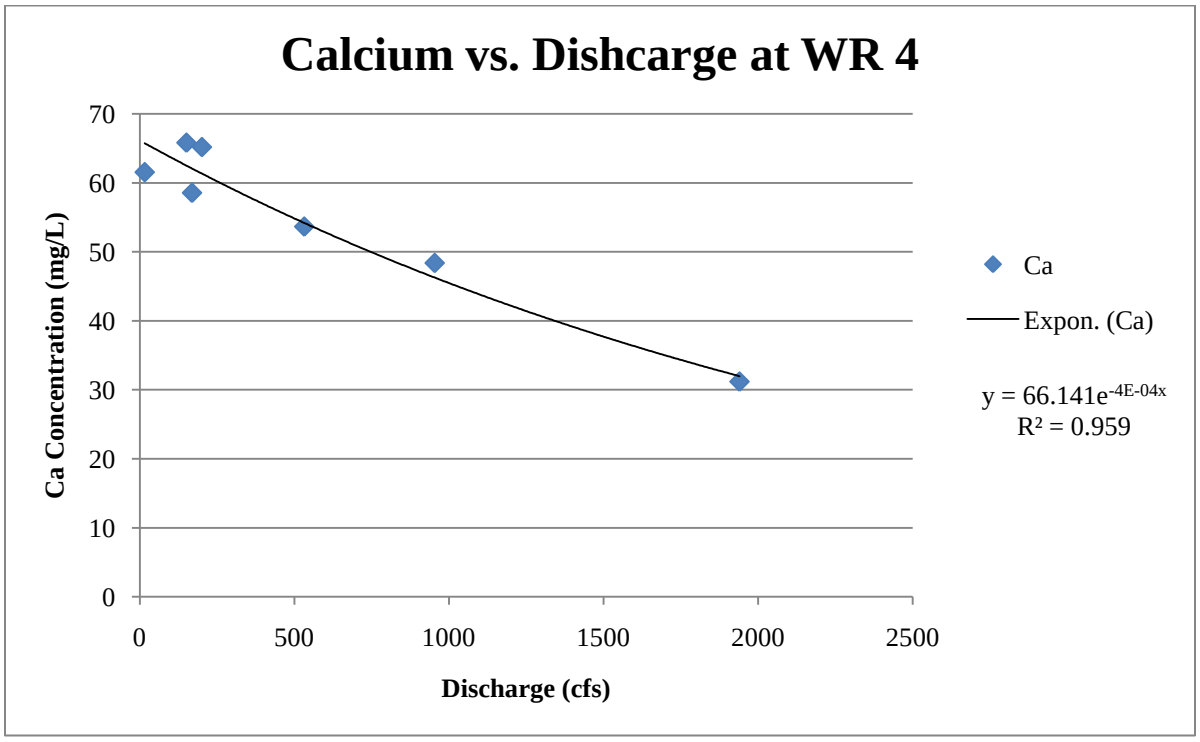

Fig. 18b. Calcium vs. discharge at WR 4, excluding last two sample runs.

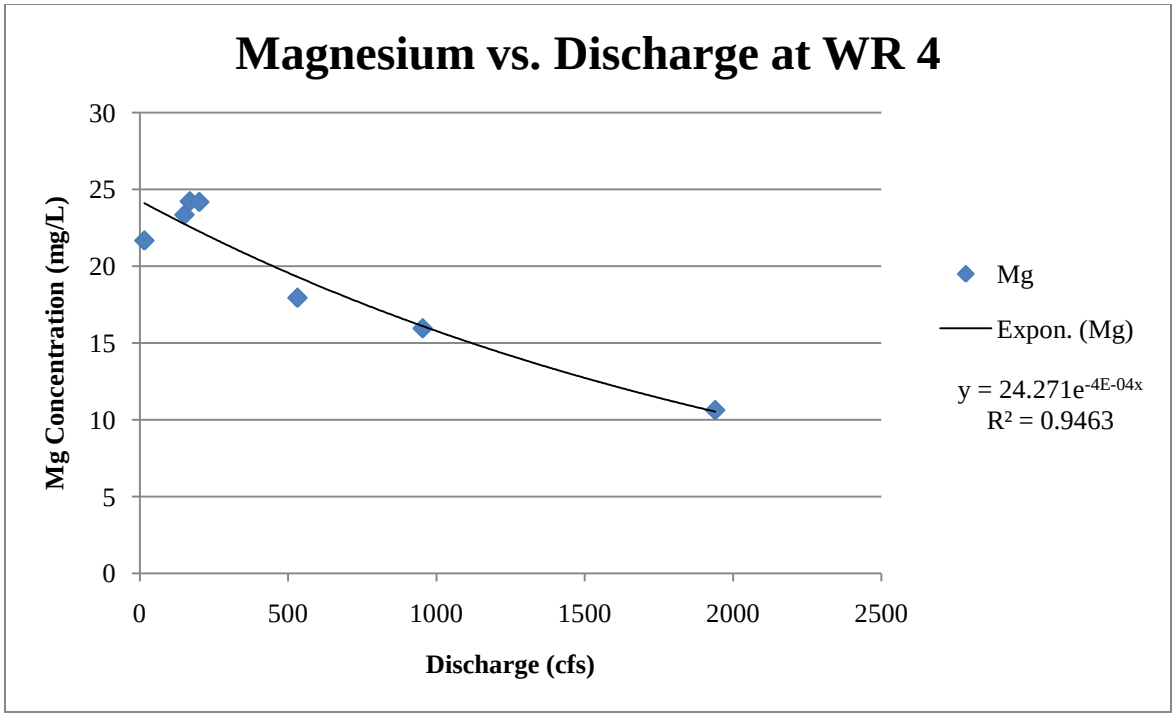

Fig. 18c. Magnesium vs. discharge at WR 4.

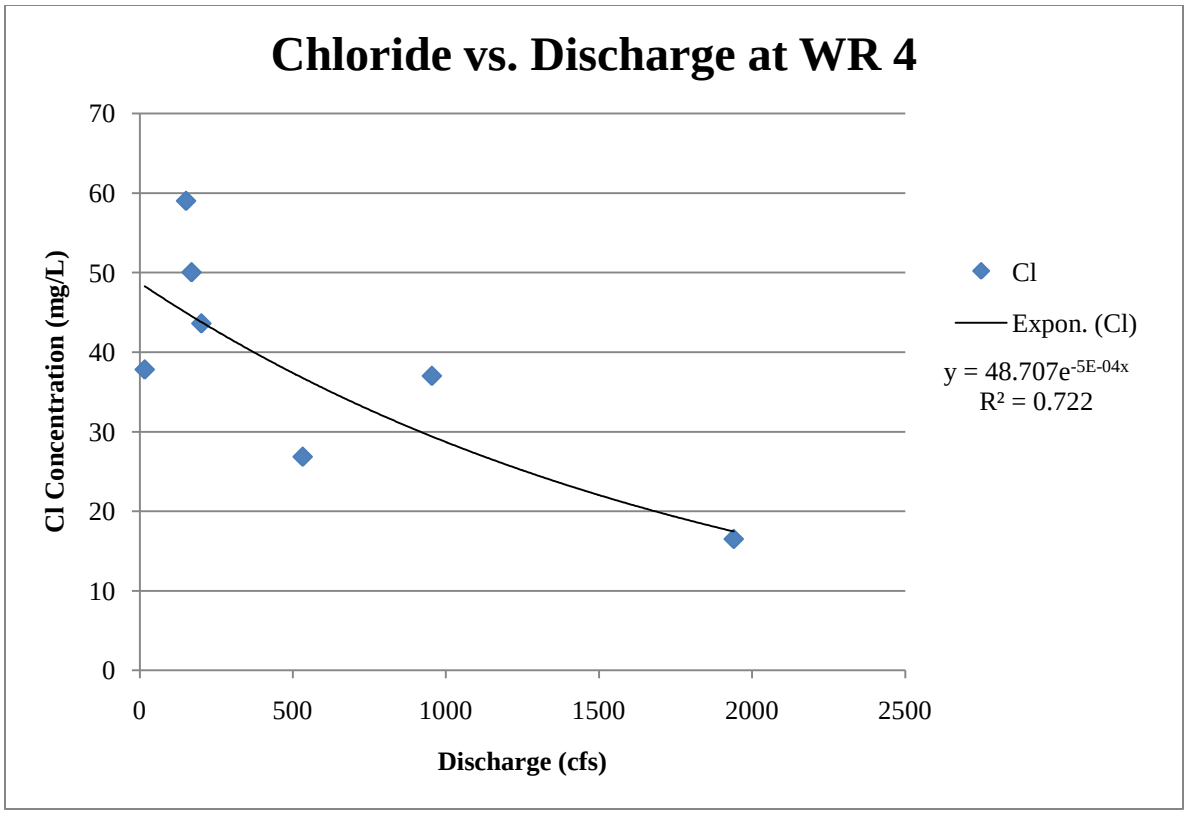

Fig. 18d. Chloride vs. discharge at WR 4.

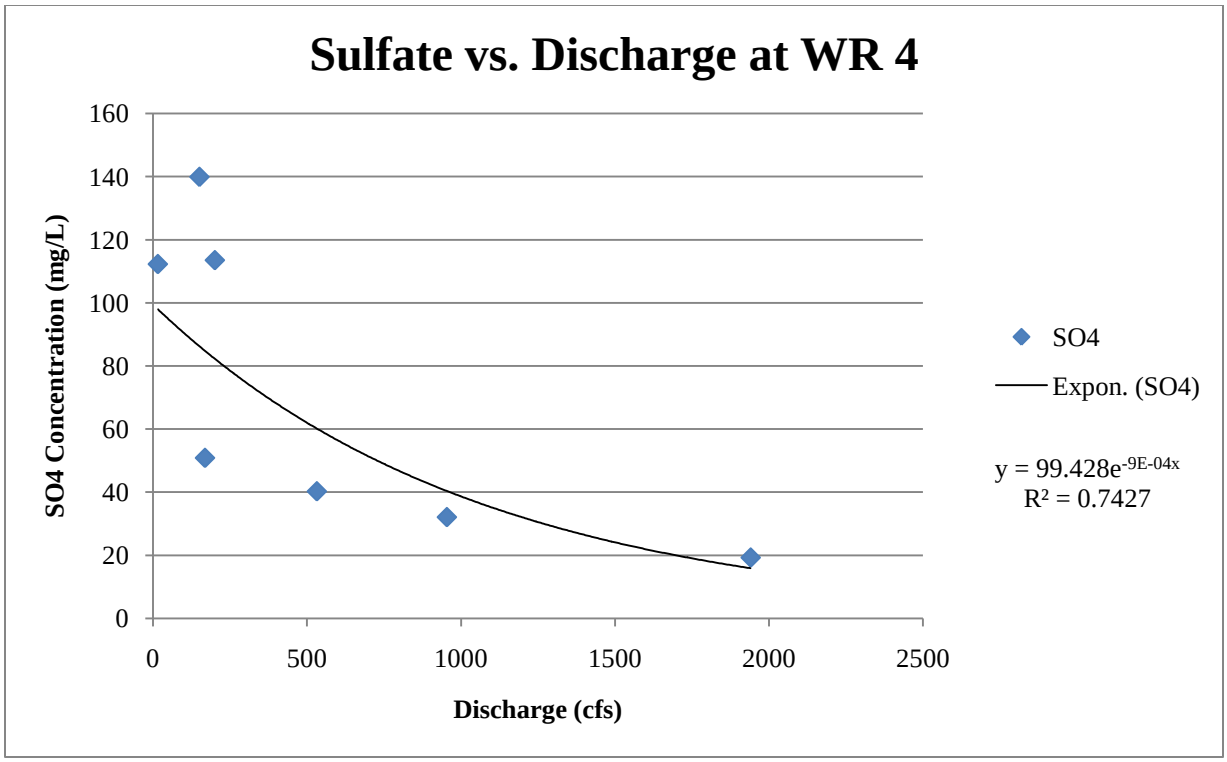

Fig. 18e. Sulfate vs. discharge at WR 4.

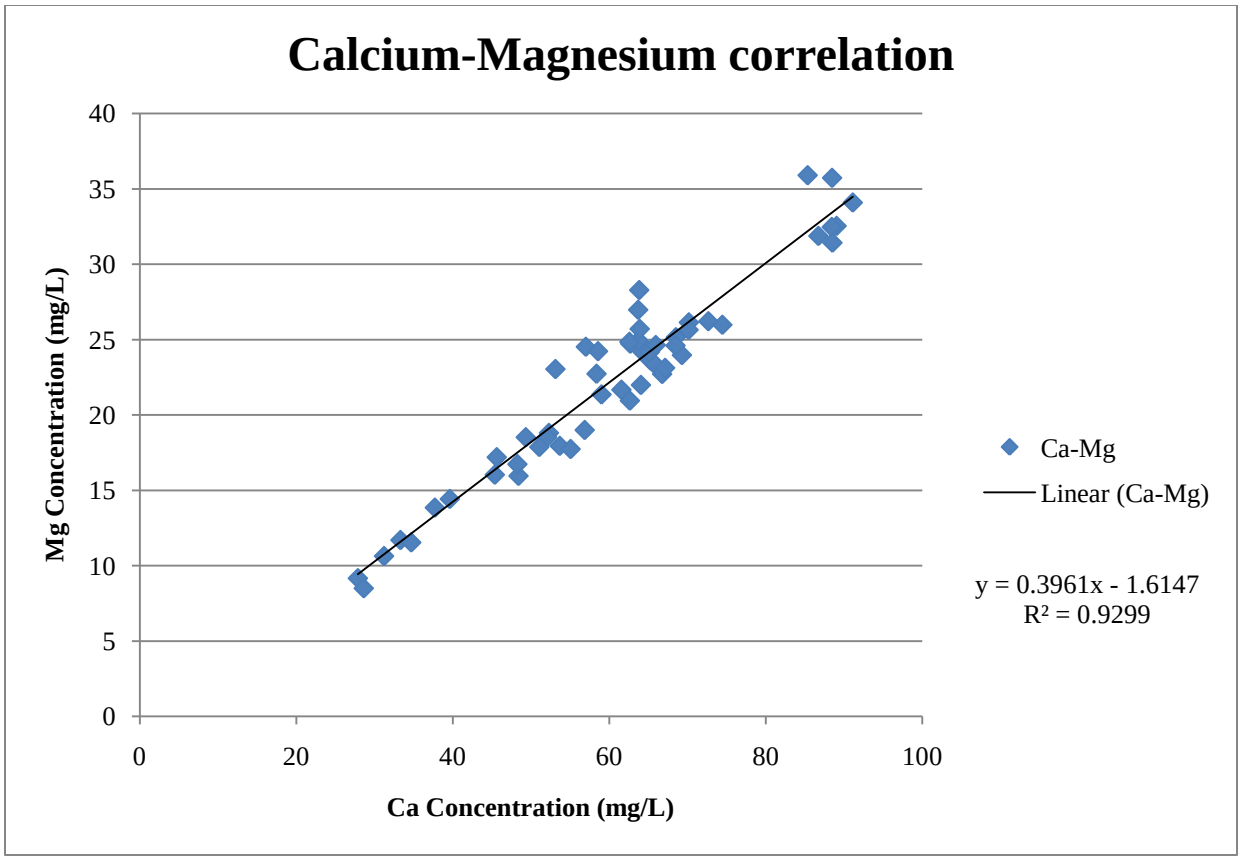

Fig. 19. Calcium-magnesium correlation. The relationship is expected and seen to be very strong since the main source of these two ions is the local geology.

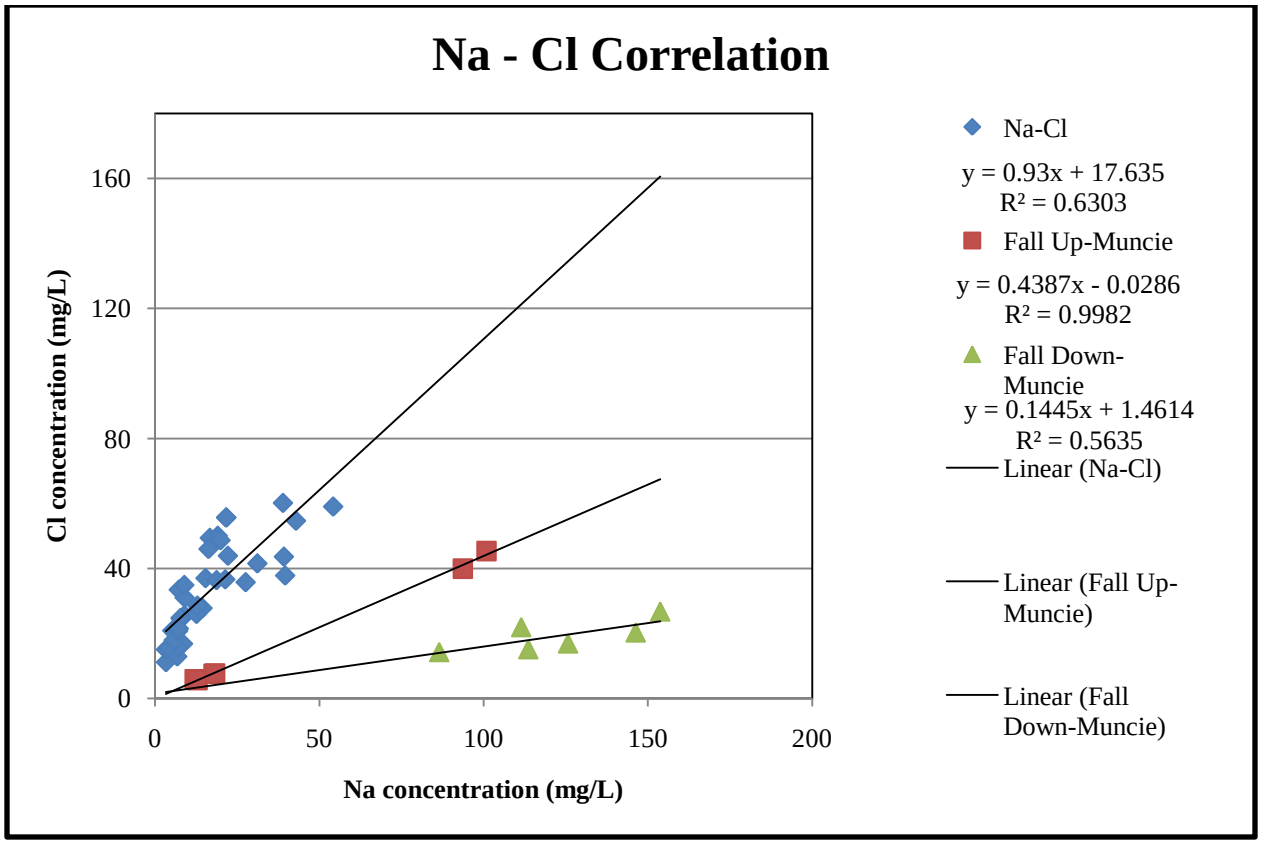

Fig. 20a. Sodium-chloride correlation for all sample sites. The relationship is weakly linear.

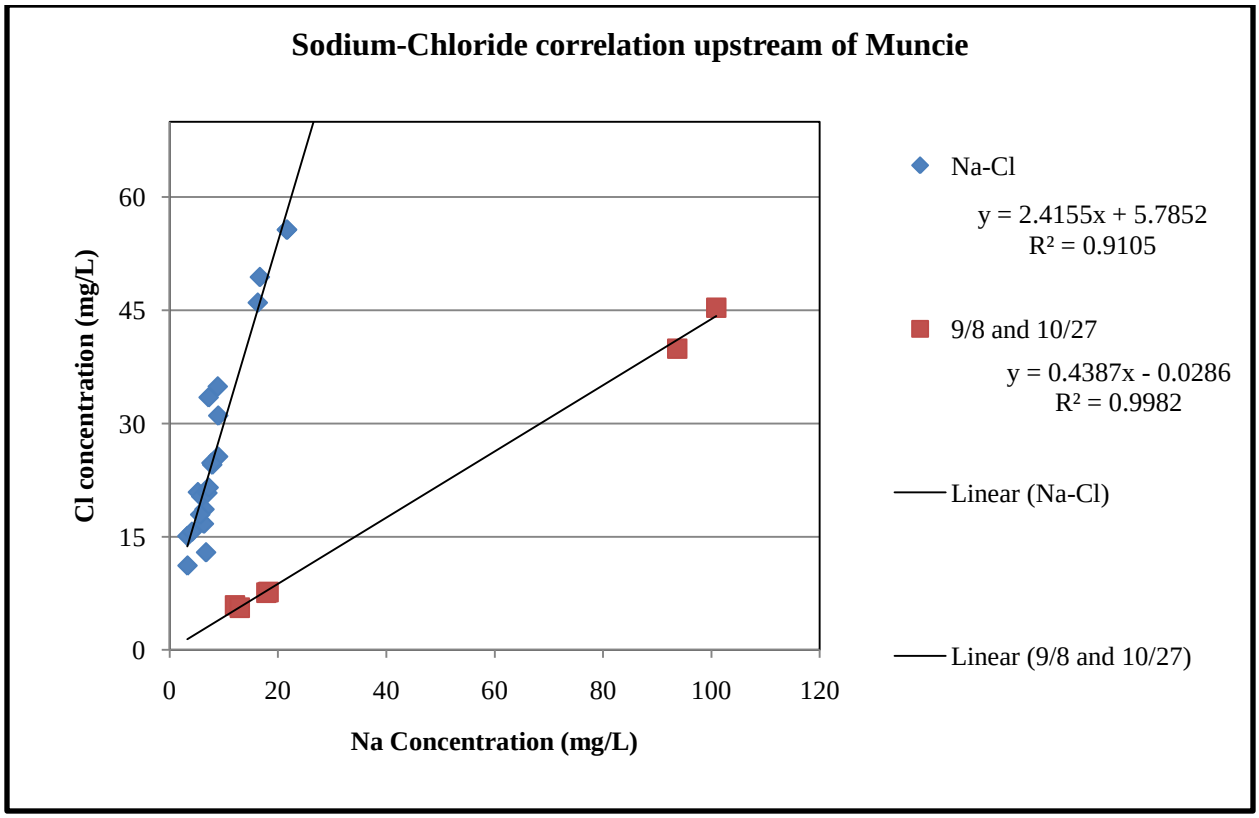

Fig. 20b. Sodium-chloride correlation for the first three WR sample sites. Relationship is now strongly linear suggesting that most of the sodium and chloride entering the river is in the sodium-chloride form.

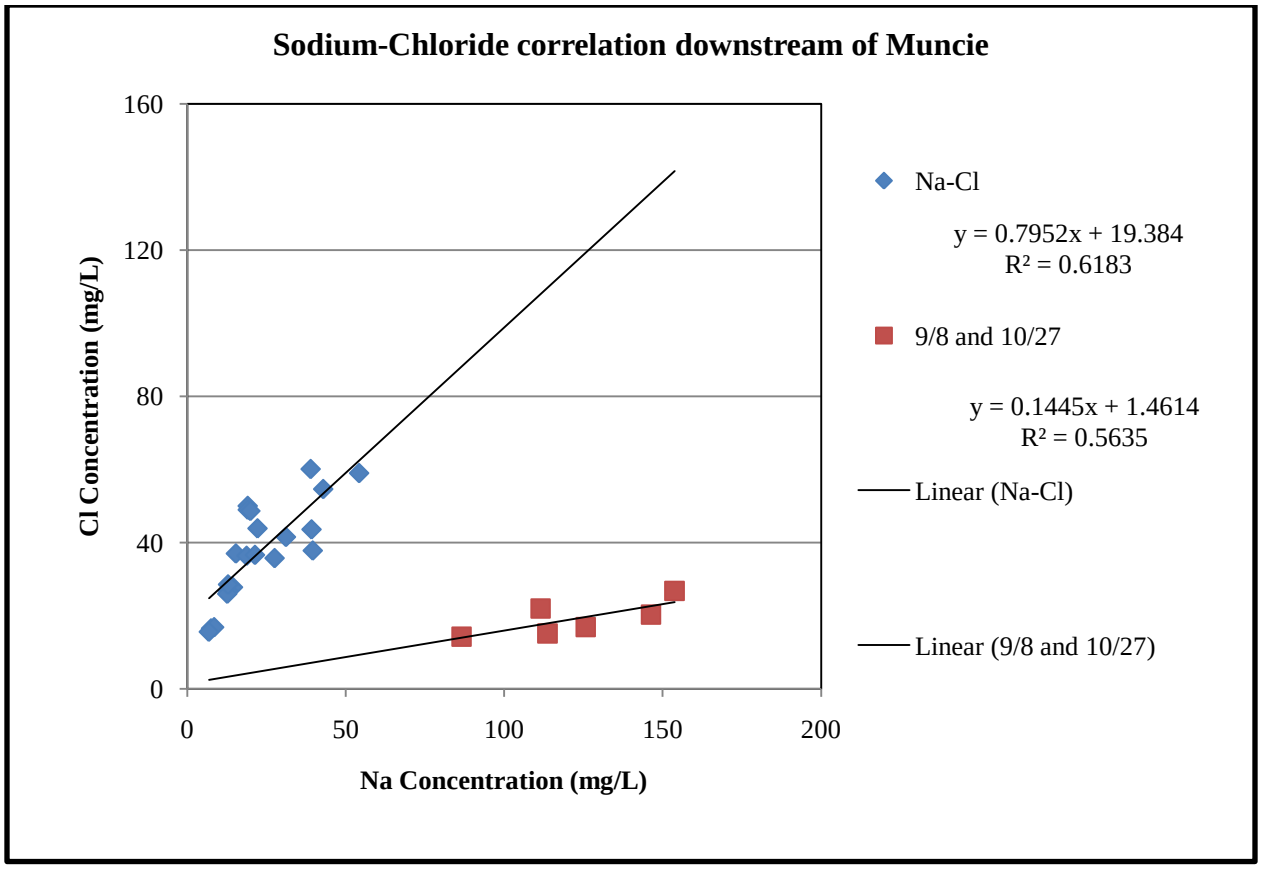

Fig. 20c. Sodium-chloride correlation for second three sample sites, downstream of Muncie. The relationship is weakly linear.

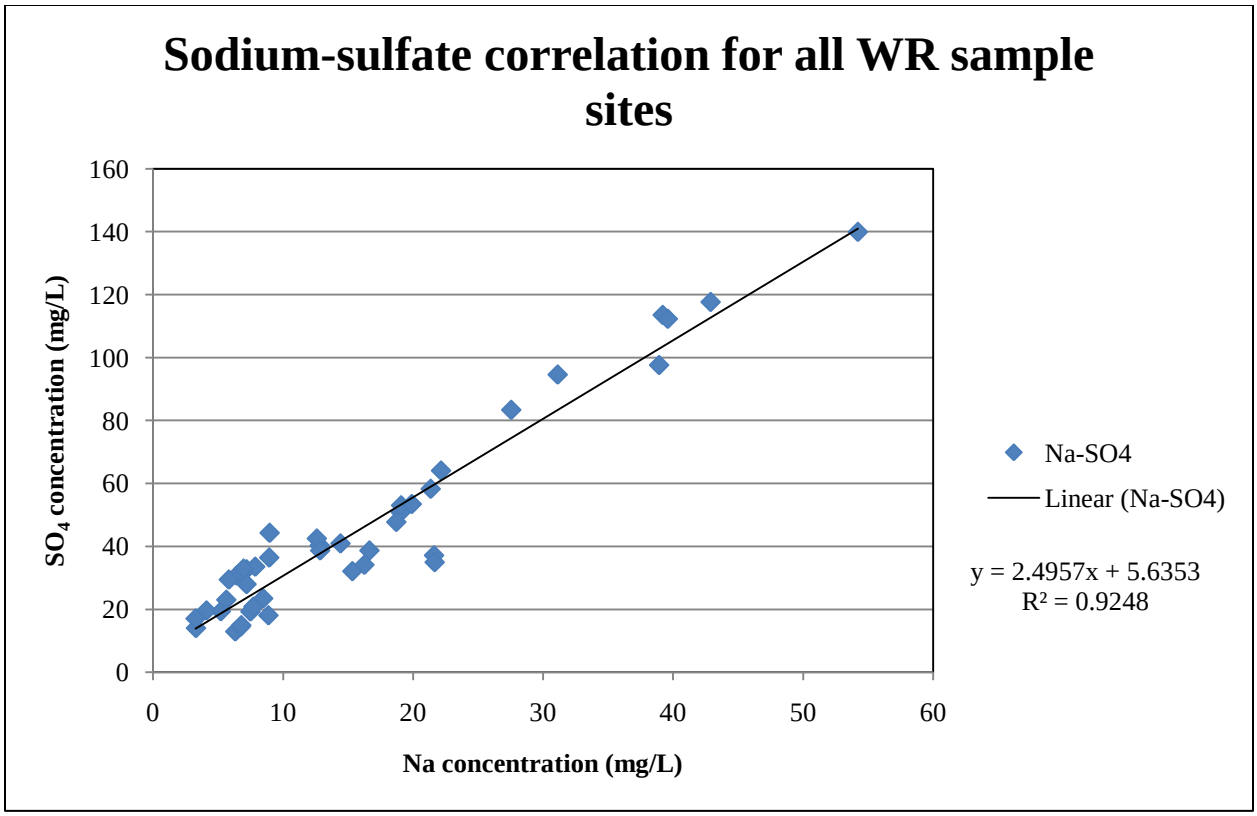

Fig. 21a. Sodium-sulfate correlation for all White River sample sites. The relationship is strongly linear.

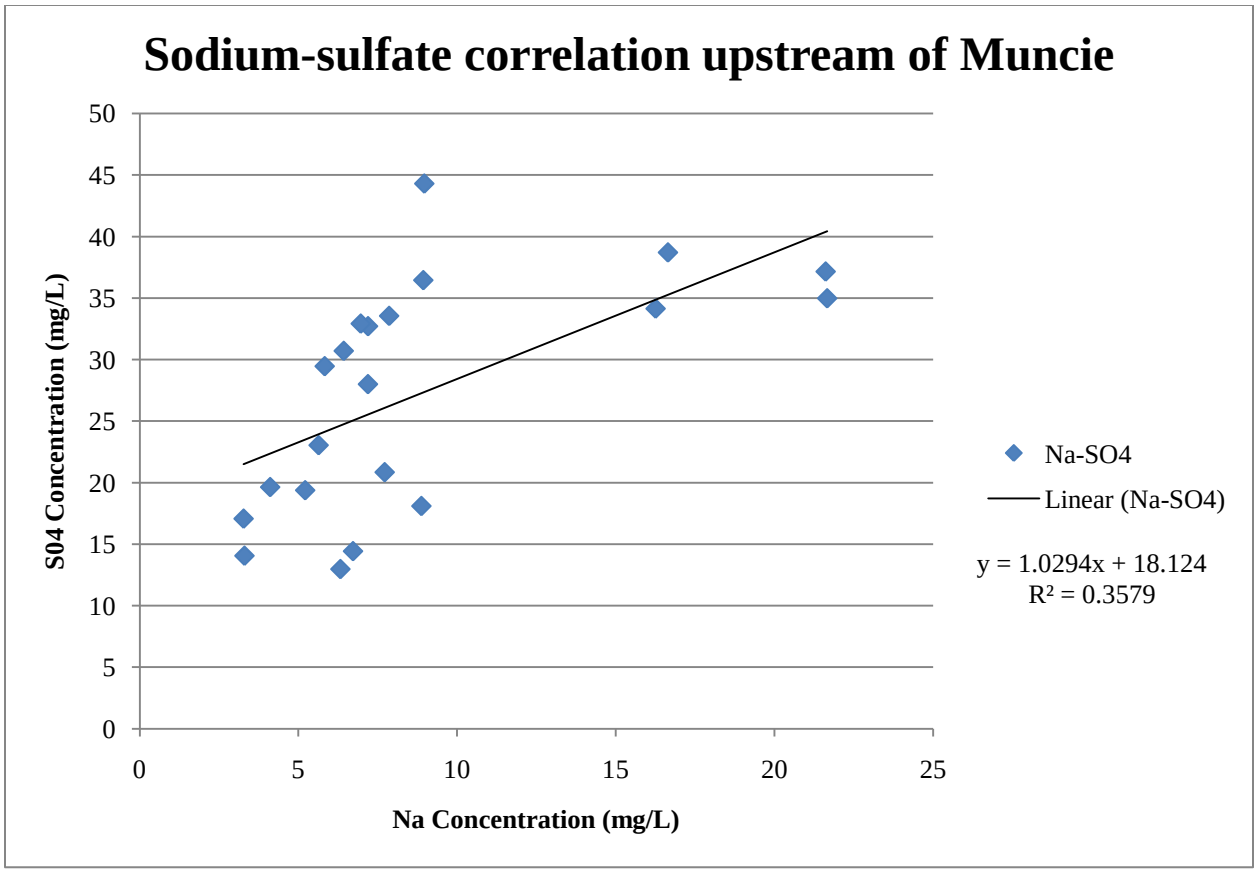

Fig. 21b. Sodium-sulfate relationship upstream of Muncie. Very weak linear relationship suggests that sulfate is not entering the water in the sodium-sulfate form.

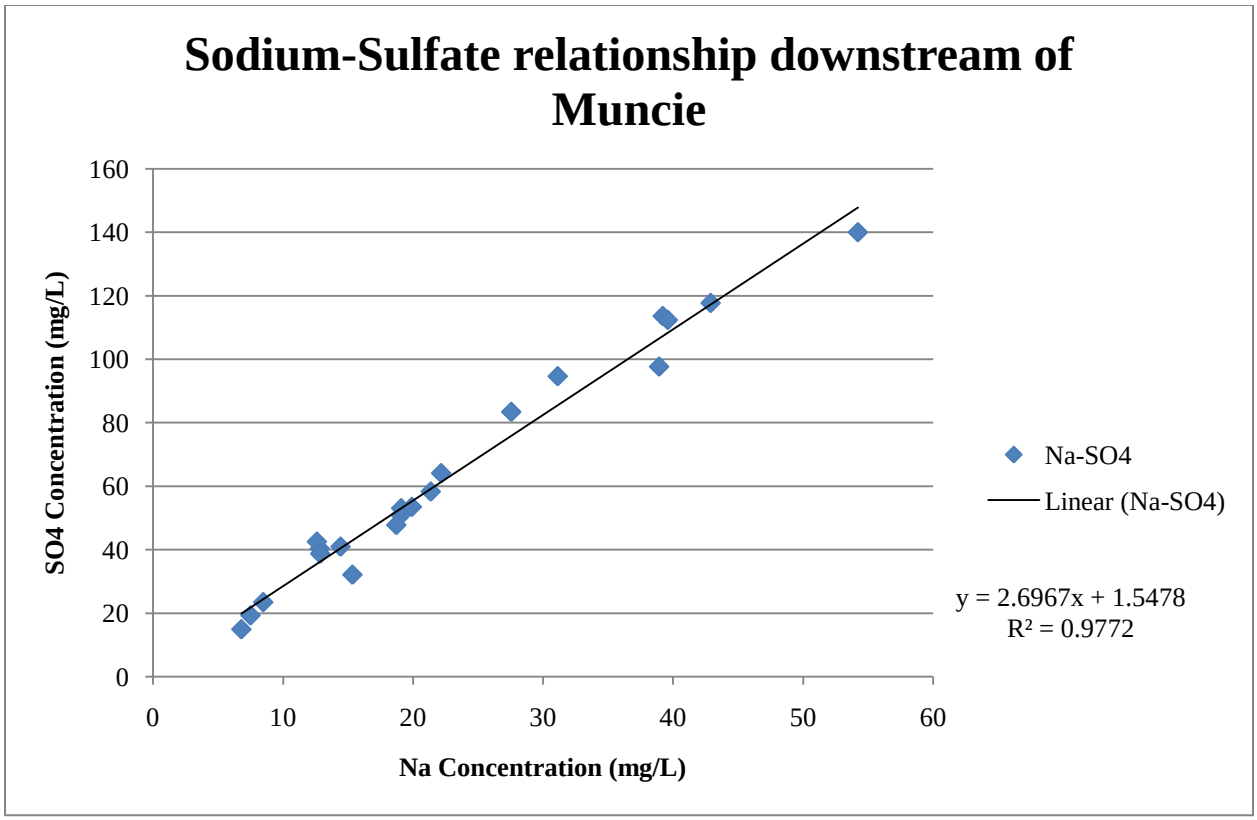

Fig. 21c. Sodium-sulfate relationship downstream of Muncie. Stongly linear relationship suggests that these ions are entering the river as sodium-sulfate.

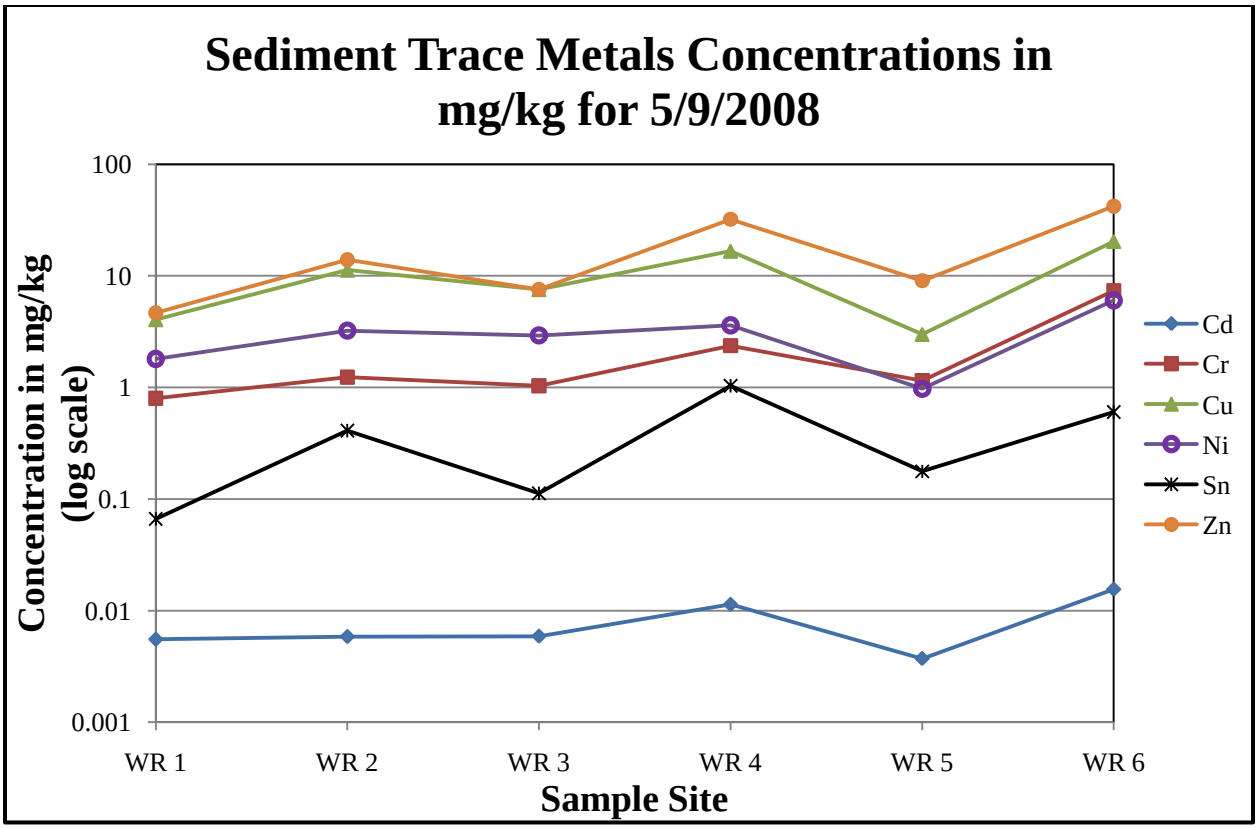

Fig. 22. Sediment trace metals concentrations collected on 5/9/2008. These six trace metals are characteristic of urban pollution.

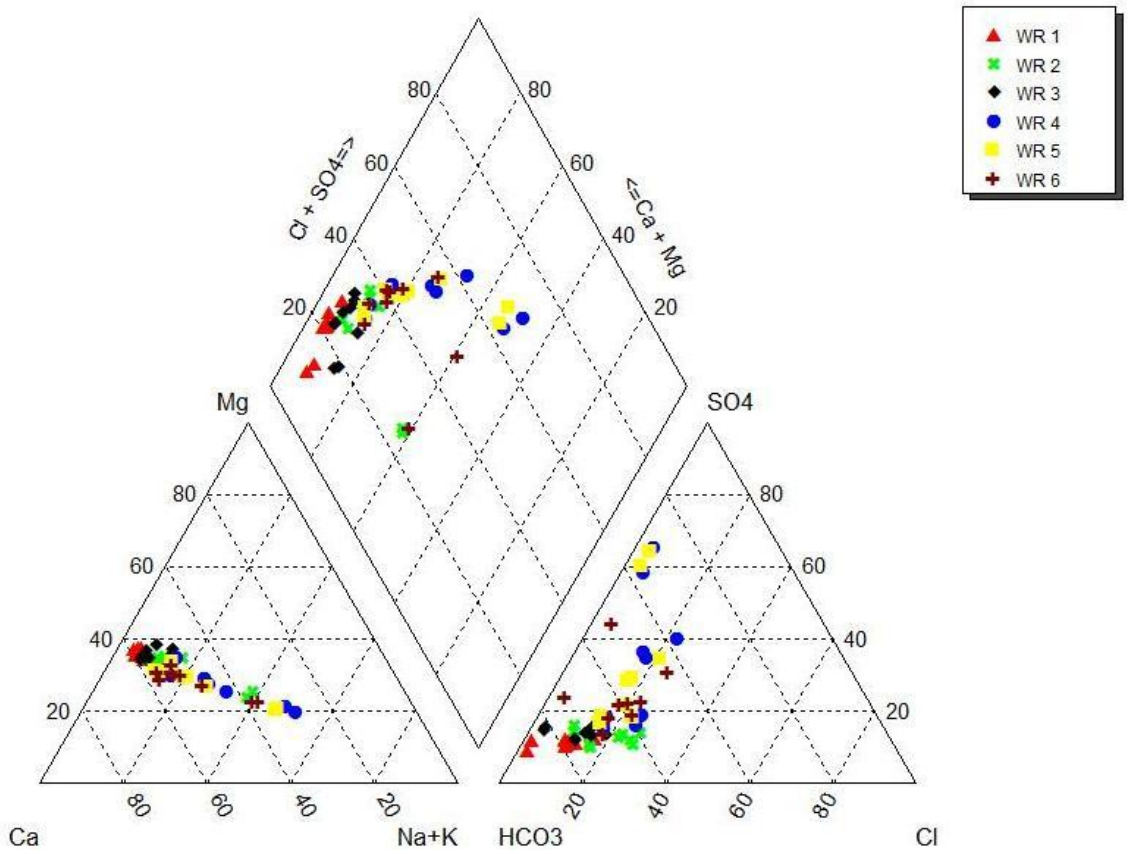

Fig. 23. Piper Diagram for White River samples.